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FIELD EVALUATION OF METHODS OF COLLECTION AND ANALYSIS OF AIRBORNE PESTICIDES. VOLUME I. FIELD EVALUATION AND ANALYSIS

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Syracuse University

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Field Evaluation of Methods of Collection and Analysis of Airborne Pesticides

Volume I – Field Evaluation and Analysis

EPA Contract CPA 70–145
SURC Project L1073–05

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SURC

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for the

Environmental Protection Agency
Research Triangle Park, North Carolina

Details of illustrations in this document may be better studied on microfiche

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ABSTRACT

An eight station experimental airborne pesticides monitoring network was established using a prototype design pesticide collection system. Sampling was conducted for a 12 month period according to the random schedule of the National Air Surveillance Network at Winter Haven, Florida, Lubbock, Texas and in New York State at Buffalo, Naples, Rome, Jordan, Lafayette, and Syracuse.

Of the possible 208 samples, 202 were collected, giving a 97% collection rate. Four of the six samples missed were due to electrical power failures caused by blizzard conditions. Only two were lost due to equipment failure.

Analysis of the samples showed that, of the 202 samples collected, pesticides were found in 68 samples (33.5%), and that they were collected, either singly or in combination on 17 sampling days out of 26 possible (65.4%). The chronological occurrence of the pesticides indicated seasonal appearance beginning in March and ending in October for the southern stations, and from April through September in the New York stations.

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FIELD EVALUATION OF METHODS OF COLLECTION AND ANALYSIS OF AIRBORNE PESTICIDES

SECTION I

CONCLUSIONS

1. The field evaluation of the prototype field sampling instrument for the collection of airborne pesticides proved to be quite successful. The 12 month operation of the eight station experimental network demonstrated the feasibility of using the instrument for routine sampling.

2. The pesticide collection module used in this project proved to be an effective method of collection of airborne pesticides. By having the capability of collecting suspended particulate matter as well as adsorbing pesticide vapors, the unit may prove to be a valuable tool in assessing the mode of appearance of pesticides in the ambient atmosphere.

3. Pesticides other than the study compounds may be collected with a high degree of efficiency. Ethion, for example, was found in high concentrations at Winter Haven, Florida.

4. The collection media proved to be amenable to the separation and cleanup procedures outlined in Pesticide Analytical Manual Volume I, "Methods Which Detect Multiple Residues." The analytical procedures outlined in the manual were adapted for routine use in the laboratory.

5. The results of the analysis showed that the levels of the study pesticides found at each sampling site were of the same magnitude as found in other published studies. Due to the increased volume of air sampled with the prototype system, a larger quantity of each pesticide present was collected, thereby making pesticide confirmation less difficult.

6. The sampling locations provided positive information regarding pesticide concentrations at each site when sampling was conducted according to a random sampling schedule. Obvious seasonal pesticide usage trends were discernable at each location. Pesticides were found at essentially the same concentration level and with the same frequency in both urban and rural areas.

SECTION II

RECOMMENDATIONS

1. Since pesticides were found in both urban and rural areas on a seasonal basis, with no levels found above the estimated lower level of detection from November through February, sampling frequency should be increased, but on a random basis, during the growing season at locations in areas of anticipated higher pesticide usage.

2. Sampling sites should be selected according to several factors, including pesticide usage and anticipated human exposure. Several sites should be located in remote areas to provide baseline pesticide concentration data.

3. The field evaluation of the pesticides collection module has demonstrated that a wide range of types of pesticides is collected with the cottonseed oil-coated glass beads as the vapor phase collection media. Other pesticides and other airborne organic compounds, which may be collected, should be investigated for analytical and collection efficiencies. Selection of the pesticides should be based on available scientific literature data, as well as pesticide usage in the location of interest.

4. Although cottonseed oil has proven to be a good liquid absorbing media, it has proven to be somewhat difficult to work with analytically and as a natural product must constantly be checked for contamination. Potential replacements should be screened to replace the cottonseed oil as the liquid phase, but no natural oil from crops treated with pesticides should be investigated. It is recommended that only synthetic liquids be used. Selection should be made on the basis the capability of the liquid to absorb a wide range of pesticides, and be amenable to routine laboratory procedures for separation, cleanup, and analysis.

5. The pesticide collection system has the capability of providing data regarding pesticides adsorbed on suspended particulate matter as well as gas phase pesticides. Due to the nature of this project, separate analysis of the particulate matter collected on the filter and gas phase pesticides in the cottonseed oil coated glass beads were not performed. Separate analysis would provide some indication of the mode of existence and transport of airborne pesticides in the ambient atmosphere.

6. Low temperature collection efficiency studies should be performed to determine if the collection module is effectively collecting airborne pesticides at lower ambient temperatures. This may be a factor in finding lower-than-detection-limit quantities in the samples collected from November through February.

SECTION III

INTRODUCTION

The objective of this project was to conduct a field evaluation of the pesticide collection system developed under Contract CPA 70-15 (1). In order to satisfy the objective, field sampling equipment was fabricated at the Syracuse University Research Corporation (SURC) based on the prototype developed by SURC. The field sampling equipment was constructed from off-the-shelf hardware available commercially, but assembled at SURC.

An eight station experimental monitoring network was established and samples collected according to the National Air Sampling Network random sampling schedule. Field sampling instruments were placed at selected sampling sites, and assembled pesticide collections modules, which could be quickly installed or removed in the field by volunteer field sampling personnel, were shipped by normal means. After collection, the samples were shipped directly to SURC for analysis of fourteen pesticides: DDT and its derivatives, total 2,4-D acids as the methyl ester, aldrin, endrin, heptachlor, heptachlor epoxide, parathion, malathion, and methyl parathion. A complete description of the pesticides is given in Table 1.

TABLE 1

Test Pesticides

Airborne Pesticides Study

Common Name	Chemical Name
Aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8,-dimethanonaphthalene
o,p´-DDD	2-(o-chlorophenyl)-2-(p-chlorophenyl)-1,1-dichloroethane
p,p´-DDD	2,2-bis(p-chlorophenyl)-1,1-dichloroethane
o,p´-DDE	2-(o-chlorophenyl)-2-(p-chlorophenyl)-1,1-dichloroethylene
p,p´-DDE	2,2-bis(p-chlorophenyl)-1,1-dichloroethylene
o,p´-DDT	2-(o-chlorophenyl)-2-(p-chlorophenyl)-1,1,1-trichloroethane
p,p´-DDT	2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane
Endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-endo-5,8-dimethanonaphthalene
Heptachlor	1,4,5,6,7,8,8a-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
Heptachlor epoxide	1,4,5,6,7,8,8a-heptachloro-2,3-epoxy-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
Malathion	S-[1,2-bis(ethoxycarbonyl)ethyl]O,O-dimethyl phosphorodithioate
Methyl parathion	O,O-dimethyl-O-p-nitrophenyl phosphorothioate
Parathion	O,O-diethyl-O-p-nitrophenyl phosphorothioate
2,4-D	2,4-dichlorophenoxyacetic acid

A basic analytical scheme was developed for the analysis of pesticides collected in the field samples. The scheme followed was one commonly used for the determination of multiple pesticide residues in fatty material since the vapor phase pesticides were trapped in a collection media of cottonseed oil-coated glass beads. Various analytical studies, including recovery of each pesticide from the analytical scheme, the efficiency of collection of each pesticide by the pesticides collection module, and storage stability of test samples, were performed in conjunction with the analysis of the field samples.

SECTION IV

BASIS FOR AIRBORNE PESTICIDES MONITORING DEVELOPMENT

Monitoring of the ambient atmosphere for airborne pesticides has been conducted for many years, especially in areas of heavy pesticide usage. A multiplicity of sampling techniques exist, and may be categorized into four basic methods: (a) collection on an inert filter media, (b) collection in a liquid absorbing media, (c) collection on a solid adsorbent media, and (d) collection using a combination of the above.

The first technique, collection on an inert filter media, was used by Tabor (2) who analyzed samples collected by high volume air samplers which used a glass fiber filter mat to collect airborne particulate matter.

Liquid absorbing systems have been used extensively. Two typical systems used are those of Miles (3) whose system was composed of a series of modified Greensburg-Smith impingers, while Willis, et.al. (4), used a flask equipped with a gas dispersion tube. Both of these systems used ethylene glycol as the absorbing media. Bamesberger and Adams (5) adapted the impinger technique in a unique way by developing a rotating disk impactor-midget impinger combination to collect gaseous and aerosol herbicides.

A dearth of information exists regarding the use of solid adsorbents alone as a method of airborne pesticide collection. The literature shows that solid adsorbents are generally used in combination with liquid absorbents. A Florisil column was used by Yule (6), while Stanley (7) used alumina.

The most successful collection devices have been those which are composed of the separate components listed above. The most recent, and elaborate, collection device assembled for routine airborne pesticide sampling was that developed by Stanley, et.al. (7).

Although recovery studies for test pesticides have shown that the collection efficiency of each of the above methods is acceptable, each system is limited to a low sampling rate, from 0.1 cubic foot to 1 cubic foot per minute, and the absorbing solution volume decreases drastically after a few hours due to evaporation of the absorbing media. At these low flow rates, the volume of air sampled during the short time period that sampling takes place does not provide enough suspended particulate matter to weigh accurately so that particulate concentrations may be calculated for correlation purposes.

In order to overcome these basic problems and others which evolve during routine sampling with liquid absorbing systems, criteria were developed and followed in order to simplify field monitoring for airborne pesticides. The criteria were basically comprised of the following points:

1. A field sampling shelter would be utilized which would remain in the field, would be simple to operate and be mechanically stable.
2. A collection device would be developed which would be simple, easy to install in the field, and withstand the rigors of shipping.
3. The collection device would not require assembly in the field by servicing personnel, thereby minimizing handling in the field.
4. The collection device would be designed so that it would efficiently collect a wide range of pesticides and provide samples which could readily be analyzed on a routine basis for pesticides using existing analytical multiresidue techniques.

SECTION V

AIRBORNE PESTICIDES MONITORING UNIT

The monitoring unit developed for field sampling of airborne pesticides was an outgrowth of a prototype field sampling instrument designed previously at the Syracuse University Research Corporation.(1) Since comparable units were not available commercially, the samplers were fabricated at SURC. A complete airborne pesticides system is shown in Figure 1.

The shelter was a standard aluminum high volume air sampler shelter used by EPA in its National Air Quality Surveillance Network, modified to provide added stability and rigidity. An aluminum plate [14 3/8" x 14 3/8" x 3/8" with a 1" flange (1/4" maximum bend radius at the edges)] was substituted for the sheet aluminum support plate supplied with the shelter. A second plate, identical to the first, was installed near the base of the seven-day skip timer, and attached to the legs of the shelter to give the unit added rigidity. Four aluminum angles (3' x 2" x 2") were attached to the ends of the legs to provide adequate wind bracing.

The top plate formed the support for the air blower unit, flow-meter, and pesticide collection module, as well as the necessary piping. These parts are connected as shown in the schematic diagram in Figure 2. With the top of the shelter down and secure, air is

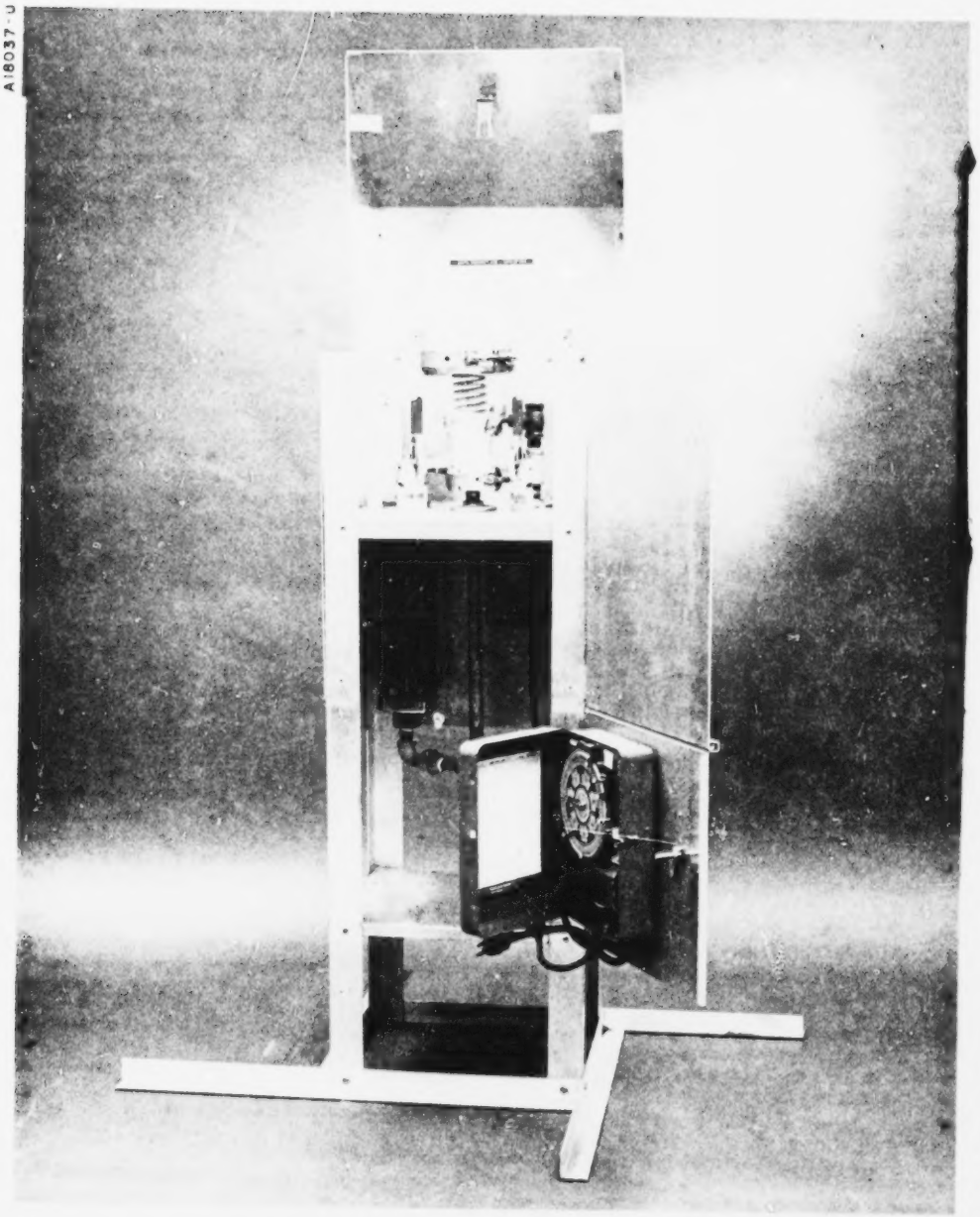


FIGURE 1 COMPLETE AIRBORNE PESTICIDE SAMPLER

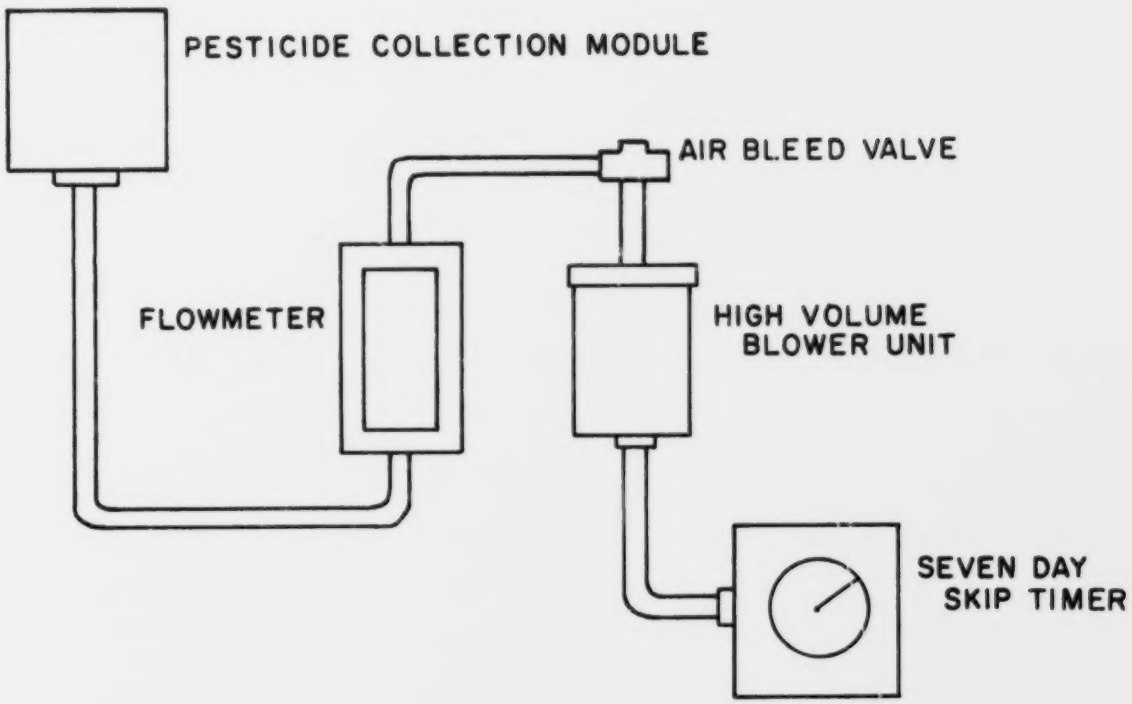


FIGURE 2 SCHEMATIC DIAGRAM OF AIR SAMPLING SYSTEM

drawn through the pesticide collection module by a high volume air sampling blower unit. The air flow rate is set at 10 CFM, as indicated on the flowmeter, by adjusting the 1/2" gate valve, which is open to the atmosphere. The blower unit pulls 10 CFM through the sampling module while running at its 40 - 60 CFM capacity. This arrangement insures a longer running lifetime for the motor unit. The motor is turned on and off by the seven-day trip timer.

A description of the basic parts and suppliers is given in Table 2 for the shelter unit.

The heart of the sampling unit is the pesticide collection module. An assembled module and its component parts are shown in Figure 3. The basic module shell consists of a 4" I.D. by 2" I.D. Pyrex pipe reducer, 17" long. The 4" I.D. end is 3 1/4" long with a 3/4" long constriction to the 2 3/4" long 2" I.D. portion. A description of the individual parts and the method of their assembly follows:

A 3 7/8" circle of 10 mesh stainless steel screen is placed inside the reducing portion of the glass pipe. A 1/8" diameter seven helix aluminum spring 8 1/2" long and 2" overall diameter is inserted into the reducer.

A 4 3/4" diameter glass fiber filter mat is carefully placed over a 4 5/8" diameter, 40 mesh stainless steel screen. This combination is placed in a 4" I.D. stainless steel shelled coupling

TABLE 2

Basic Parts and Suppliers for the Airborne Pesticides

Monitoring Unit Shelter Only

Part and Description	Vendor
Aluminum Shelter Hi Vol Air Sampler, Model GMWL2000, Less Filter Holder Capacitor 2004 Motor Brushes 33252 Timers, 7 Day Skip	General Metal Works, Inc. 8368 Bridgetown Road Cleveland, Ohio 45002 513-914-2229
Varea-Meter (Air Flow Meter) Tube No. WY-1/2-40-G-5 Float No. 1/2-G-10V1-24 Float Nat'l. 316 Stainless End Fitting - Brass, Vertical Screwed Connections Tube Retainer - Penton "O" Rings - Buna N Frame Style - Slip-on Covers Scale Length - 5 inches, detached Scale Units - SCFM Fluid - Air, 10 SCFM S.G. 1.0, Temp. 70°F, Press, A Atmos.	Wallace and Tiernan 25 Main Street Belleville, New Jersey 07101 201-759-8000

TABLE 2 (Cont'd)

Part and Description	Vendor
Aluminum Plate 15 3/4" x 15 3/4" x 3/8"	Local Hardware Supplies
Clamps, DE - STA - Co. #207SB	" " "
Floor Flange, Gal. 1/2" x 3"	" " "
1/2 Gate Valves	
Piping: Elbows (3)	" " "
Union (1)	" " "
Tee (1)	" " "
Nipples (6)	" " "
Pipe, two (4" long, 1/2" I.D.)	" " "
Pipe, one (12" long, 1/2" I.D.)	" " "

equipped with a Teflon inner flange, with the filter mat facing outward. A 4 5/8" diameter 10 mesh stainless steel screen is inserted into the coupling over the 40 mesh stainless steel screen. The coupling is then placed over the rim of the reducer with the spring centered on both 10 mesh screens. The top 10 mesh screen provides added support for the glass fiber filter mat, while holding the screen in the reducer firmly in place.

At this point 140 ml of 3 mm smooth-surface Pyrex glass beads, previously coated with 3 ml of refined cottonseed oil, is added to the reducer at the 2" I.D. end. The 140 ml volume of beads provides a bed approximately 2 3/4" long in the reducer.

A 2 1/4" diameter stainless steel screen is placed in a 2" I.D. stainless steel shelled coupling which has a Teflon inner flange. The coupling is placed over t· · rim of the 2" I.D. end of the reducer, and the coupling gently tightened to prevent the coupling from coming loose.

A description of the basic parts and supplies is given in Table 3 for the sampling module.

The assembled collected module is placed in a specially designed shipping container shown in Figure 4. This box, 9" square, 11 1/2" high, is constructed of welded aluminum plate, is shown in Figure 4 with the pesticide collection module in place. The lid has affixed a removeable 4" O.D. Teflon coated flange mounted inside. In the bottom of the box

TABLE 3

Basic Parts and Suppliers for the Airborne Pesticides

Monitoring Unit Sampling Module Only

Part and Description	Vendor
Reducer and Increaser, 4" x 2", Code 4222	Corning Glass Works Corning, New York or Local Corning Representative
Coupling, Stainless Steel Shell Coupling, 2", Code 20009	
Bolt, 4", Code 4408	
Insert, 4", Code 4308	
Springs to Specification	Local Supplier (matched on premisis for proper tension)
10 Mesh Stainless Steel Screen	Local Supplier
40 Mesh Stainless Stell Screen	" "
Glass Beads, Pyrex, 3mm diameter Cat. No. 11-312A	Fisher Scientific Co. Local Office

A18038-U

FIGURE 3 PESTICIDE COLLECTION MODULE COMPONENTS

FIGURE 4 SHIPPING CONTAINER WITH PESTICIDE COLLECTION MODULE

is a 2" O.D. Teflon coated flange which is also removable. These flanges are centered on the lid and in the box so that the collection module fits snuggly and level over both flanges. When the module is in place and the lid clamped into place, the module is held completely immobile. Additional shockproofing is provided by lining the inside edges and lid areas with 1/4" neoprene strips.

A description of the basic parts for the shipping case is given in Table 4.

The shipping boxes are mailed or sent by other means to the field servicing personnel for installation. The collection module is carefully removed from the shipping case and the new module immediately placed in the sampling shelter. The module is placed onto a 2" O.D. machined stainless steel flange, shown in Figure 5. The installed collection module, with the retaining clamps in place, is shown in Figure 6.

The used collection module is placed in the shipping case at the time that the new module is removed, and the lid immediately put into place, and shipped back to the laboratory for analysis.

Detailed operating procedures for the pesticide monitoring unit, the preparation of the airborne pesticides collection module, and shipment of the pesticide collection module are given in Appendices A, B, and C respectively.

TABLE 4

Basic Parts and Suppliers for the Airborne Pesticides

Monitoring Unit Shipping Case Only

Part and Description	Vendor		
Aluminum Plate for Sides, Top, and Bottom, 3/8" thick, cut to size	Local Hardware Suppliers		
Latches, Snap Clamps, Handle	"	"	"
Teflon, 6" x 6" x 3/8", Wt. 1 1/8 lb.	"	"	"
Teflon 1" x 2 1/2" x 1/16" thick	"	"	"
1/4" Neoprene (17 lbs.)	"	"	"

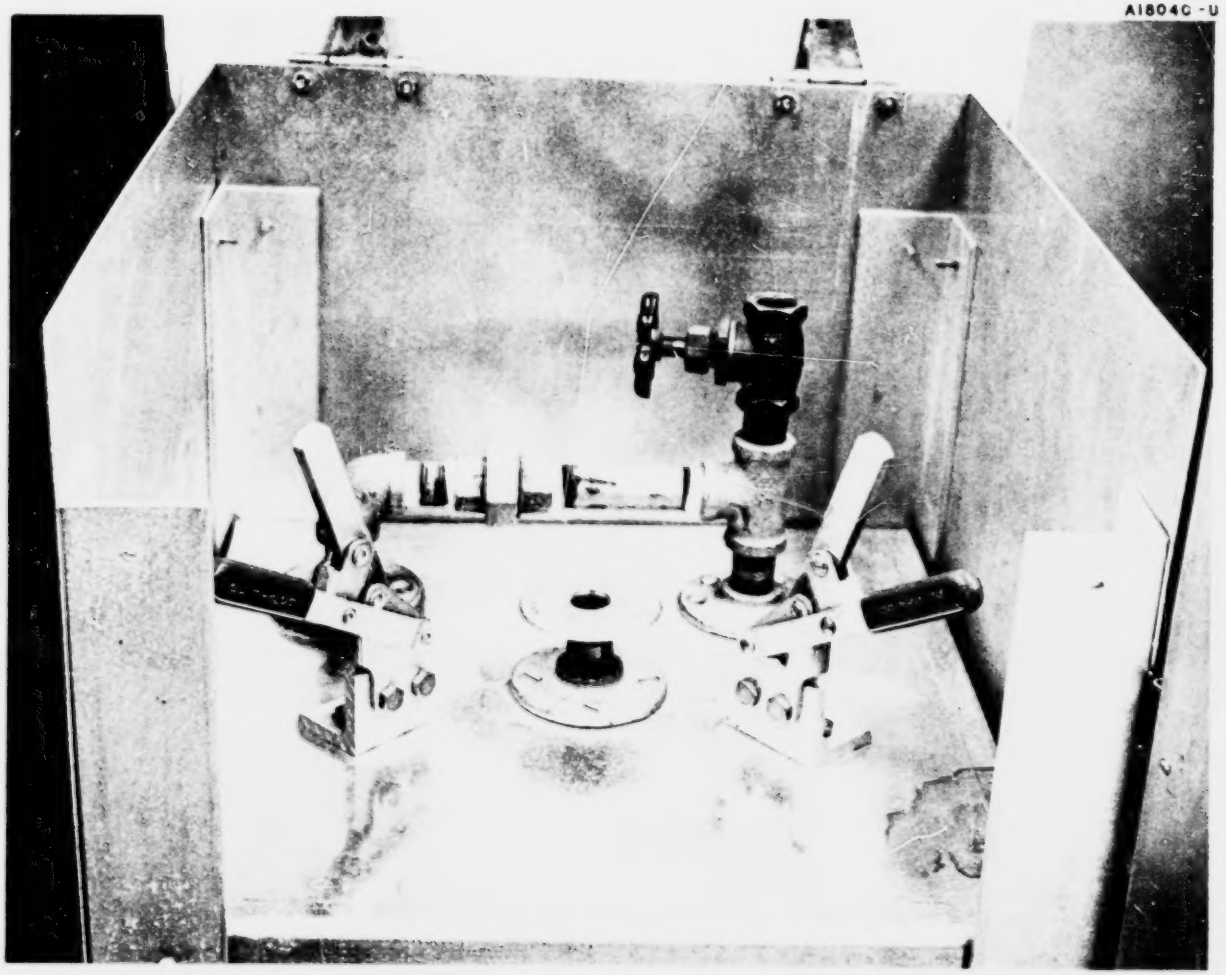


FIGURE 5 PESTICIDE COLLECTION MODULE COMPARTMENT WITHOUT MODULE

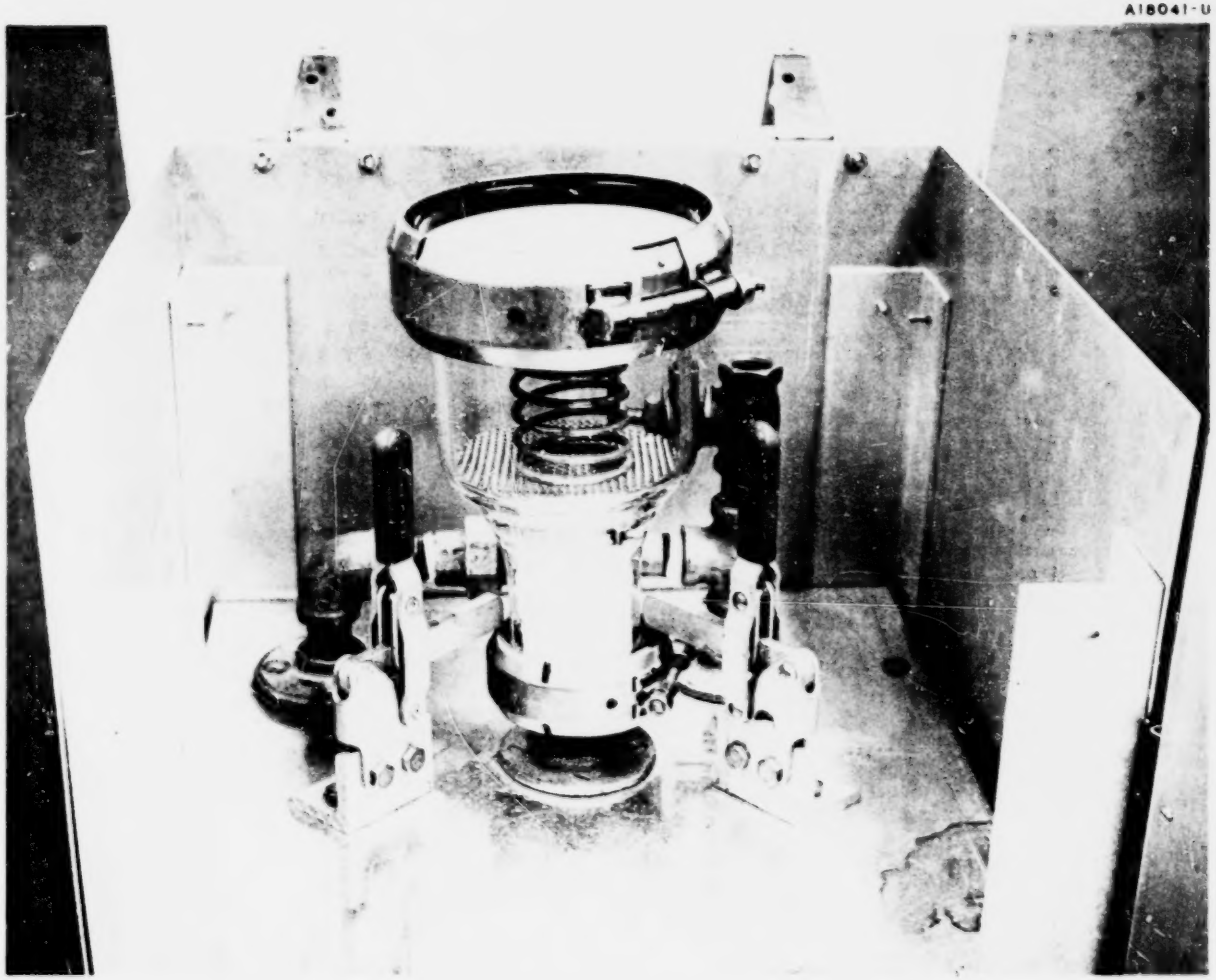


FIGURE 6 PESTICIDE COLLECTION MODULE COMPARTMENT WITH MODULE INSTALLED

SECTION VI

MONITORING AIRBORNE PESTICIDES

Eight locations were selected as sampling sites for the pesticide monitoring unit. The locations were selected on the basis of potential study pesticide use, availability of volunteer servicing personnel, and availability of an adequate sampling site. One site was located in Winter Haven, Florida, one in Lubbock, Texas, and six in New York State at Buffalo, Jordan, Lafayette, Naples, Rome, and Syracuse. A detailed description of each site is given in Table 5.

Establishment of the network began in November, 1970, and was completed in mid-December, 1970.* One pesticide monitoring unit was shipped or hand delivered to each site, and assembled by SURC personnel. Representatives of each volunteer servicing organization were present during the assembly of the unit, and were instructed in the proper procedures for servicing the instrument. Detailed operating procedures and instruction are given in Appendix A. Shipping logistics, servicing personnel and addresses are given in Appendices B and C.

Monitoring was conducted for a 12 month period beginning in early December, 1970, through November, 1971. Sampling was conducted using the random sampling schedule used in the National Air Surveillance Network. The schedules for 1970 and 1971 are shown in Tables 6 and 7 respectively.

Table 5

Site Identification for Airborne Pesticides Monitoring

Location	Station Code	
Winter Haven, Florida	10 4880 01	Department of Air and Water Pollution Control, 225 Avenue D, N.W., Winter Haven. The station is located on a one story building in the center of the city, approximately three miles from citrus groves. There are no large obstructions in the area.
Buffalo, New York	33 0660 01	Buffalo Museum of Science, Humbolt Parkway, Buffalo, New York. The site is near the center of the city in a predominantly residential district. The station is located on a four story building and is an existing NASN site. There are no obstructions that would affect sampling.
Rome, New York	33 5060 01	Rome State School. The station is on a two story building located in a rural truck farming area. There are no large obstructions in the area.
Jordan, New York	33 5100 01	Jordan Grade School, Jordan, New York. The station is on a three story building located within the village limits but adjacent to general farmland. There are no obstructions in the area.
Lafayette, New York	33 5100 02	McLusky Orchards on U.S. Route 20, approximately 2 miles west of Lafayette, New York. The station is located on a one story building. The site, surrounded by apple orchards, is located on the northeastern side of a hill and commands a view of metropolitan Syracuse located in the same valley approximately 10 miles due north.

Table 5 (Cont.)

Location	Station Code	
Naples, New York	33 5120 01	Widmer Wine Cellars in Naples. The station is located approximately 300 yards west of N.Y. Route 21. A stack from an oil-fired boiler is approximately 80 feet south of the station and 60 feet above, but the stack showed no visible emmissions. The site is surrounded by vineyards.
Syracuse, New York	33 6620 01	City of Syracuse Water Maintenance Building, Beech Street and Erie Boulevard. The station is located on a two story building in the center of the city, in a predominantly commercial area. This is an existing NASN station.
Lubbock, Texas	45 3340 01	No. 5 Fire Station, 10th Street and Zenith Avenue. The sampling station is mounted on a one story building in a residential area on the east side of the city. There are no large obstructions that could influence the sampling. Cotton fields surround the city and the station is within one-half mile of cotton fields to the east.

Table 6

1970

National Air Surveillance Networks

Random Sampling Schedule

Sampling Period	Sampling Day				Date Period Ends	
1	Fri.	Jan.	2		Jan.	10
2	Tues.	Jan.	13		Jan.	24
3	Thurs.	Jan.	29		Feb.	7
4	Sat.	Feb.	14		Feb.	21
5	Wed.	Feb.	25		Mar.	7
6	Mon.	Mar.	9		Mar.	21
7	Sun.	Mar.	22		Mar.	31
8	Wed.	Apr.	8		Apr.	18
9	Sun.	Apr.	19		May	2
10	Thurs.	May	7		May	16
11	Sat.	May	23		May	30
12	Tues.	June	2	NOTE: ALL SAMPLING	June	13
13	Mon.	June	15	TIMES ARE FROM MID-	June	27
14	Sat.	July	4	NIGHT TO MIDNIGHT	July	11
15	Tues.	July	14	(0000 to 2400)	July	25
16	Thurs.	July	30		Aug.	8
17	Mon.	Aug.	10		Aug.	22
18	Wed.	Aug.	26		Sept.	5
19	Fri.	Sept.	11		Sept.	19
20	Sun.	Sept.	20		Sept.	30
21	Wed.	Oct.	7		Oct.	17
22	Tues.	Oct.	20		Oct.	31
23	Fri.	Nov.	6		Nov.	14
24	Sun.	Nov.	15		Nov.	28
25	Sat.	Dec.	5		Dec.	12
26	Mon.	Dec.	14		Dec.	26

If a scheduled sample is missed, every effort should be made to collect one before the end of the period, preferably on the same day of the week.

EXCEPTION: No two samples should be collected in the same calendar week.

Table 7

1971

National Air Surveillance Networks

Random Sampling Schedule

Sampling Period	Sampling Day				Date Period Ends	
1	Tues.	Jan.	5		Jan.	9
2	Wed.	Jan.	13		Jan.	23
3	Fri.	Jan.	29		Feb.	6
4	Thurs.	Feb.	11		Feb.	20
5	Sat.	Feb.	27		Mar.	6
6	Mon.	Mar.	8		Mar.	20
7	Sun.	Mar.	21		Mar.	31
8	Sun.	Apr.	4		Apr.	17
9	Wed.	Apr.	21		May	1
10	Tues.	May	4		May	15
11	Fri.	May	21		May	29
12	Sat.	June	5	NOTE: ALL SAMPLING	June	12
13	Mon.	June	14	TIMES ARE FROM MID-	June	26
14	Thurs.	July	1	NIGHT TO MIDNIGHT	July	10
15	Fri.	July	16	(0000 to 2400)	July	24
16	Mon.	July	26		Aug.	7
17	Sun.	Aug.	8		Aug.	21
18	Wed.	Aug.	25		Sept.	4
19	Sat.	Sept.	11		Sept.	18
20	Tues.	Sept.	21		Sept.	30
21	Wed.	Oct.	6		Oct.	16
22	Sat.	Oct.	23		Oct.	30
23	Thurs.	Nov.	4		Nov.	13
24	Mon.	Nov.	15		Nov.	27
25	Fri.	Dec.	3		Dec.	11
26	Sun.	Dec.	12		Dec.	25

If a scheduled sample is missed, every effort should be made to collect one before the end of the period, preferably on the same day of the week.

EXCEPTION: No two samples should be collected in the same calendar week.

SECTION VII

EXTRACTION, SEPARATION, AND CLEANUP OF COLLECTED FIELD SAMPLES

Extraction, Separation, and Cleanup

When the pesticide collection module had been returned from the field, the component parts were immediately started through an extraction, separation, and cleanup procedure. The average time delay from sample collection to initial hexane extraction was approximately 6-7 days.

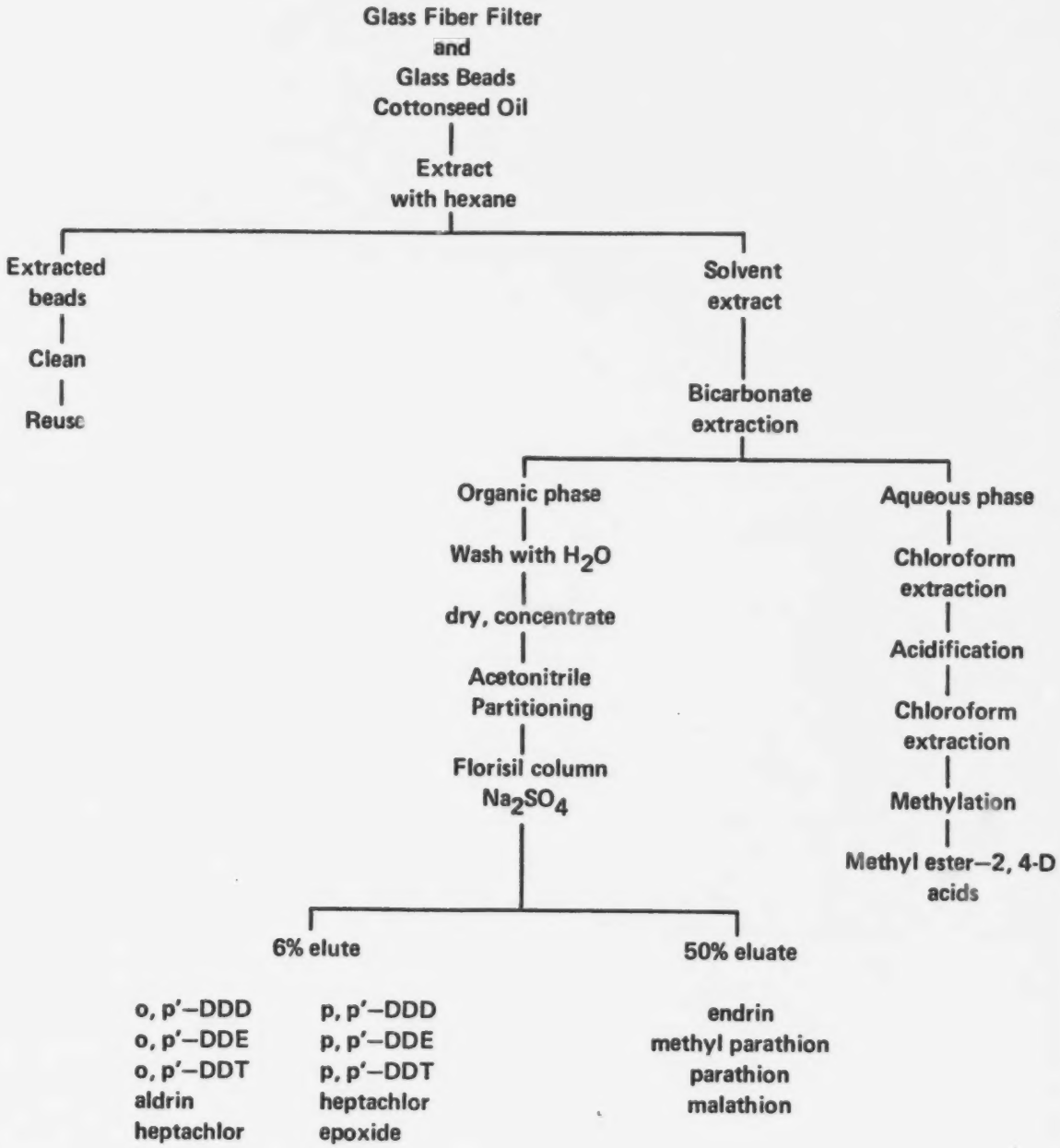
The analytical scheme, outlined in Figure 7, was patterned after methods suggested in the Pesticide Analytical Manual Volume I (8) for fatty material. Special analytical reagents, solvents, and supplies other than normal laboratory equipment are given in Appendix D. Detailed analytical procedures are given in Appendix E, but are summarized in this section.

The glass fiber filter, previously tared, was removed from the module and reweighed after being placed in a desiccation chamber at room temperature for 24 hours. The filter was weighed to the closest 0.1 mg using a Mettler Type H5 balance.

The filter mat and cottonseed oil coated beads were then placed in a Soxhlet extraction apparatus with an extraction chamber which adequately held a 123 mm x 43 mm pre-extracted cellulose filter thimble. The glass reducer, screens, and spring were carefully rinsed with hexane three

FIGURE 7

Glass Beads Coated with Cottonseed Oil and Glass Fiber Filter Separation and Cleanup Procedures



times. The Teflon surfaces of the shipping container flanges were also rinsed with hexane. All of the rinses were then placed in the extraction apparatus, and enough fresh hexane added to bring the volume of solvent to 250 ml. The beads and filter were extracted for two hours at a cycle rate of at least once every 10 minutes.

The hexane extract was extracted with a mixture of aqueous 4% sodium bicarbonate and 35 ml of ethanol. The bicarbonate aqueous phase extraction was repeated and the aqueous solutions pooled. This phase contained any 2,4-D acid or acid esters that might have been present. The aqueous phase was extracted with chloroform, and the chloroform washings discarded. The aqueous phase was acidified with 10% sulfuric acid to free the 2,4-D acids. The acidified solution was extracted with chloroform. The pooled chloroform washings were drained into a 250 ml Phillips beaker, and evaporated carefully to dryness. The dry chlorophenoxy residues were then methylated with diazomethane to form the methyl ester of 2,4-D.

The original hexane extract was washed with water, dried by passing it through anhydrous sodium sulfate, and carried through an acetonitrile partitioning procedure. The hexane solution was concentrated and carried through a Florisil column cleanup. The study chlorinated and organophosphorus pesticides were recovered from the Florisil by elution from the column with a 6% ethyl ether in petroleum

ether, and 50% ethyl ether in petroleum ether fraction.

The 6% elute contained aldrin, o,p´-DDD, p,p´-DDD, o,p´-DDE, p,p´-DDE, o,p´-DDT, p,p´-DDT, heptachlor, and heptachlor epoxide. The 50% eluate contained endrin, malathion, methyl parathion, and parathion. No 15% ethyl ether-petroleum ether eluate was collected since malathion divides between the 15% and 50% eluate. As a result, malathion was eluted directly with the 50% ethyl ether-petroleum ether mixture.

The methyl ester of 2,4-D solution, and 6% and 50% eluates were adjusted to 10 ml with petroleum ether for gas-liquid chromatographic analysis.

Pesticide Analytical Scheme Recovery Efficiencies and Recovery Normalizing Factor

During the project, sufficient data was collected from recovery studies of standards which allowed the calculation of the percent recovery which could be expected of each of the study pesticides. The average percent recovery for each pesticide is given in Table 8. The normalizing factor for each pesticide was calculated in order to adjust the determined concentrations of pesticides in the samples to 100% recovery.

TABLE 8

Pesticide Analytical Scheme Recovery
Efficiencies and Recovery Normalizing Factor

Pesticide	Recovery Efficiency, %	Normalizing Factor
Aldrin	98.9	1.01
o,p´-DDD	107.4	1.00
p,p´-DDD	95.3	1.05
o,p´-DDE	94.2	1.06
p,p´-DDE	105.2	1.00
o,p´-DDT	95.5	1.05
p,p´-DDT	95.8	1.04
Endrin	92.3	1.08
Heptachlor	90.1	1.11
Heptachlor Epoxide	108.4	1.00
Malathion	99.9	1.00
Methyl Parathion	90.6	1.10
Parathion	84.6	1.18
2,4-D, Methyl Ester	105.7	1.00

SECTION VIII

GAS CHROMATOGRAPHIC ANALYSIS OF SAMPLE EXTRACTS

The analyses of the 2,4-D methyl esters, and the 6% and 50% ethyl ether petroleum ether eluates were conducted by gas-liquid chromatography. The pesticide analyses were performed on three Micro Tek (Tracor) Model MT-220 gas chromatographs. Each unit was equipped with a Nickel-63, parallel plate, electron capture detector operated in the DC mode. Two of the units were equipped with high temperature flame photometric detectors which were operated in the phosphorus mode.

These instruments are equipped with 6 ft. by 4 mm glass U-shaped columns. Four gas chromatographic column packings were used during the course of the project. These were (a) 1.5% OV-17/1.95% QF-1 on 80-100 mesh Supelcoport, (b) 4% SE-30/6% QF-1 on 80-100 mesh Supelcoport, (c) 5% OV-210 on 100-120 mesh Gas Chrom Q and (d) 10% DC-200/1.5% QF-1 on 80-100 mesh Gas Chrom Q. Packing (a), (b), and (c) were supplied by the Perrine Primate Laboratories, while packing (d) was prepared using the mixed packing techniques described in Section 302.12 b and Section 203.12a(1), in the Pesticide Analytical Manual Volume 1 (8).

Detailed gas chromatographic operating parameters and procedures are given in Appendix F. Included in that appendix are the anticipated minimum detectable quantity of each pesticide by both electron capture detection and flame photometric detection.

Using the optimum operating parameters for a particular gas chromatographic column detector system, the sample extracts were injected into the instrument. Choice of the gas chromatographic column was predicted on the separation of the study pesticides in the 6%, 50%, and methyl ester 2,4-D extracts.

Initial screening of the 6% eluates was done on a 1.5% OV-17/1.95% QF-1 column using an electron capture detector. This column separates all of the compounds expected to be found in the 6% fraction with no overlapping peaks. For confirmatory purposes either the 5% OV-210 column, or the 4% SE-30/6% QF-1 column was used with an electron detector An injection volume of 5 µl of the 10 ml eluate concentrate was used.

Screening of the 50% eluate concentrate was done by injecting 5 µl of the 10 ml eluate concentrate onto a 1.5% OV-17/1.95% QF-1 column with an electron capture detector. This column separates malathion, methyl parathion, parathion, and endrin with no overlapping peaks. Confirmation of the organophorphorus pesticides was done by injecting 5 µl of the 50% eluate which had been further concentrated to 1 ml, onto either a 10% DC-200/1.5% QF-1 or 1.5% OV-17/1.95% QF-1 column with a flame photometric detector operated in the phosphorus mode.

The 2,4-D methyl esters were screened by injecting 5 µl of the 10 ml extract onto a 5% OV-210 column with electron capture detector. The retention time of the methyl ester was 0.69 with respect to aldrin. Aldrin injected as an internal standard with each sample. Confirmation

was done by injecting 5 µl onto either a 1.5% OV-17/1.95% QF-1 column or 4% SE-30/6% QF-1 column with an electron capture detector.

Due to the nature of the sample extracts, frequent calibration checks were made to insure that the sensitivity of each detector system was maintained, and that column performance remained at a high level of efficiency. Therefore, 5 µl of standard which gave a response roughly equivalent to the unknown was injected after each sample, but not less frequently than every two injections. Standards were injected at concentrations which gave a response in the input and output attenuation settings used for the sample.

Suspected pesticides were identified by several techniques. The most commonly used was to determine the retention time of the unknown peaks and compare them with the retention time of the standards run as calibration checks. The other technique was to use an internal standard. The suspected pesticides were then determined by comparing their relative retention ratios with the internal standard. This technique was used for all of the 2,4-D methyl ester samples.

Quantitation was done by peak height for aldrin, heptachlor, heptachlor epoxide, malathion, methyl parathion, parathion and 2,4-D methyl esters. The peaks exhibited by these pesticides are sharp and lend themselves to this type of quantitation.

The remaining study pesticides were quantitated by the peak height times width at half height since the peaks from these pesticides gave symmetrical, relatively wide peaks.

SECTION IX

PESTICIDE COLLECTION EFFICIENCIES

Introduction

The collection efficiency of the pesticide collection module for all of the test pesticides was conducted to expand the information given in a previous project (1). Initial data using p,p´-DDT, heptachlor epoxide, and methyl parathion indicated that the collection efficiency of vapor phase pesticides was the most critical facet in assessing the overall collection efficiency of the module.

Injection of quantities of these pesticides into the system while air was being sampled indicated initially some pesticide vapor was absorbed by the glass fiber mat, but after running continuously for 24 hours, no pesticide could be found on the filter (Table 9). Although some pesticide vapors may be retained on the mat, the compounds vaporize over a period of time, and must eventually be absorbed on the cottonseed oil-coated beads. The same desorption pattern may also occur for some particulate adsorbed pesticides which may be collected on the filter during sampling.

The retention of the study pesticides by the cottonseed oil may also be less than 100% for some compounds using the cottonseed oil-coated glass beads. Gage (10), using liquid impingement collection techniques found that the collection efficiency of most liquid

TABLE 9

Adsorption of p,p´-DDT, Heptachlor Epoxide, and Methyl Parathion on the Glass Fiber Filter Mat

Pesticide	Quantity Applied, ng	Quantity Found After 1 Hour, ng	Quantity Found After 24 Hours, ng
p,p´-DDT	5500	1662	0
Heptachlor epoxide	5860	251	0
Methyl parathion	5280	381	0

absorbing systems followed the relationship

$$E=V/vk\ (1-e^{-Vk/v})$$

where E is the efficiency of absorption for a volume V of air, i.e., the fraction of the vapor in volume V retained by the liquid in the absorbing media, v, is the volume of absorbing liquid, and the constant K is a measure of volatility of the vapor from solution. Gage points out that this equation shows that absorption can never be complete, and, as V increases, the exponential term of the equation tends to disappear; the efficiency is then inversely proportional to the volume of air sampled. Preliminary test data indicated that pesticide adsorption and desorption may follow the same pattern from cottonseed oil-coated glass beads, even though the volume of cottonseed oil (3 ml) is far less than the volume used in impingers such as the Greensburg-Smith type.

Determination of Vapor Phase Collection Efficiencies

The basic laboratory apparatus used for the collection efficiency studies is shown in Figure 8. This configuration is composed of identical components as the field collection device. The primary difference however, is that another Pyrex glass reducer has been placed over the primary collection canister, and a secondary collection canister has been added beneath the primary.

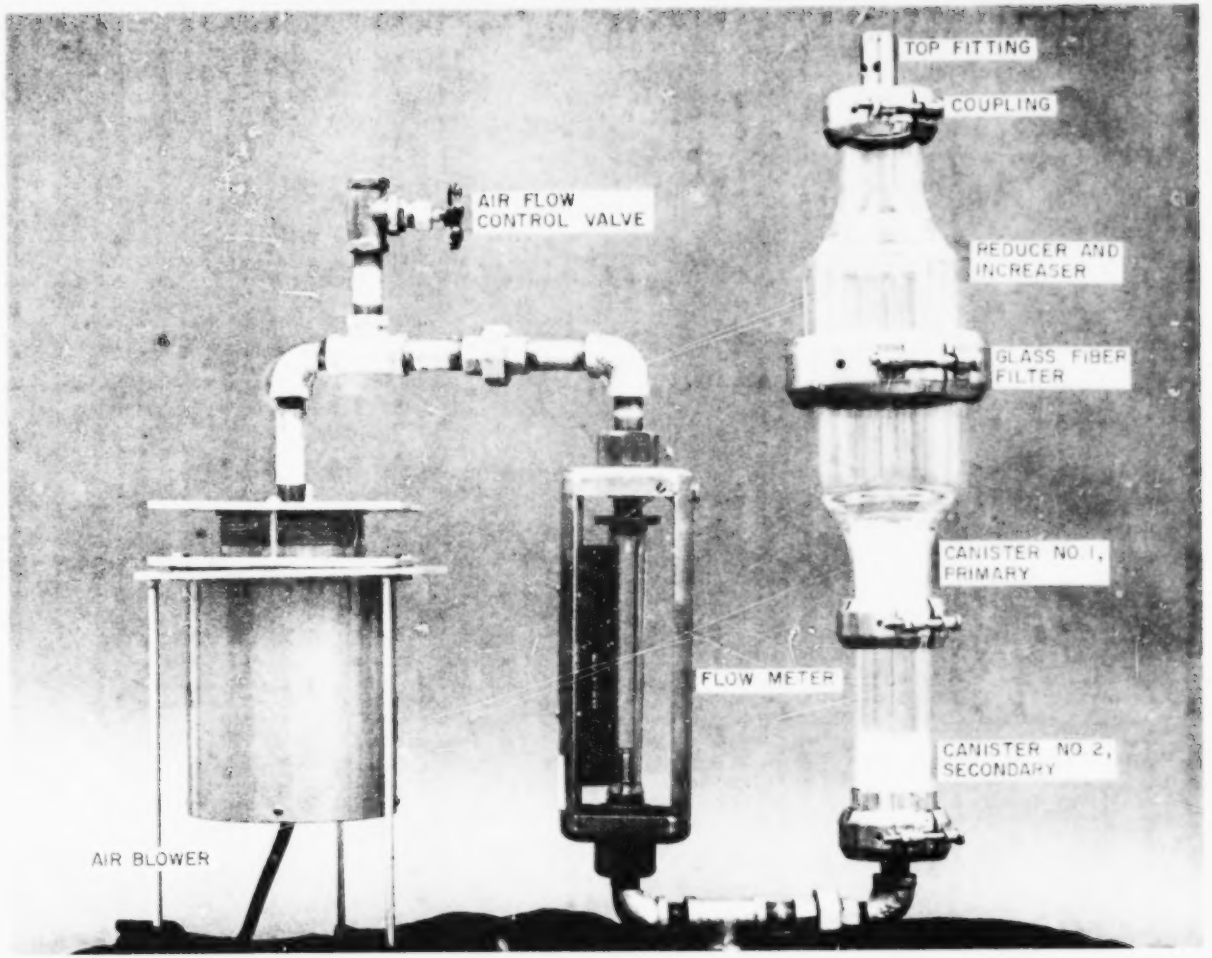


FIGURE 8

BASIC COLLECTION ASSEMBLY

A fitting has been placed at the top of the inverted reducer and is held in place by a coupling. This fitting is hollow, with a nipple-like connection entering into the side-wall. This fitting provides a means of introducing a solid aerosol from an aerosol generator into the air stream. The fitting and coupling are removed when vapor or gas studies are to be conducted.

Using the basic laboratory efficiency study assembly, 140 mls of 3 mm Pyrex glass beads coated with 3 ml of cottonseed oil was added to the primary canister and a like portion to the secondary canister. A glass fiber filter mat was placed in the 4" coupling. The coupling was then placed on the first canister, and another reducer placed in the coupling with the 2" end pointing upward. No other coupling or fitting was attached to the inverted reducer.

The blower unit was turned on, and the flow rate adjusted to 10 CFM. Using a 1 ml glass syringe equipped with a stainless steel needle, 1 ml of a carefully prepared standard containing each of the test pesticides was injected into the airstream entering the system. The injection was done dropwise, at a rate and size that the solvent evaporated before the drop came in contact with the filter. The air flow was maintained at 10 CFM at room temperature for 1 hour or 24 hours, depending on the scheduled duration of the test.

The sampling unit was carefully disassembled, and each component analyzed for the test pesticides. Calculation of the final quantities

took into account projected analytical scheme losses as described in Section VII.

Pesticide Module Collection Efficiencies

The collection efficiencies are calculated on the basis of the quantity of each pesticide collected in the primary canister composed of the glass fiber filter and cottonseed oil coated glass beads. The mean average collection efficiency found for each pesticide is given in Table 10. A normalizing factor was calculated for each pesticide so that the quantities found in the collected field samples could be adjusted to 100% collected.

Migration of Pesticides

The migration of the pesticides entering the pesticide collection module was investigated using o,p´-DDT, p,p´-DDT, methyl parathion and parathion, to determine possible desorption of pesticides as sampling time progressed throughout a 24 hour sampling period.

Using the test procedures outlined above, pesticides were injected into the influent air stream and the flow continued for 1 hour. At the end of that period, the laboratory efficiency study assembly was removed, and a fresh one installed. The same quantity of pesticide was added to the influent air stream, but the flow was continued for 24 consecutive hours. At the end of that time, the assembly was removed, and the various components analyzed for pesticide quantity.

TABLE 10

Collection Efficiencies and Normalizing Factors for the Pesticide Collection Module

Pesticide	Collection Efficiency, %	Normalizing Factor
Aldrin	67.2	1.48
o,p'-DDD	82.3	1.22
p,p'-DDD	91.5	1.09
o,p'-DDE	104.5	1.00
p,p'-DDE	78.8	1.28
o,p'-DDT	77.3	1.29
p,p'-DDT	88.5	1.13
Endrin	95.4	1.05
Heptachlor	70.6	1.42
Heptachlor Epoxide	83.6	1.20
Malathion	70.5	1.42
Methyl Parathion	78.8	1.27
Parathion	91.3	1.10
2,4-D, Methyl Ester	100.5	1.00

The results of the test are shown in Table 11. One hour after injection, a quantity of each pesticide was found on the glass fiber filter mat. Analysis of the filter after 24 hours showed that there was no pesticide present.

Analysis of the pesticides found in the primary canister had increased by approximately the same quantity as had been found on the filter after the one hour run. Analysis of the secondary canister gave results which showed an increase in the quantity of pesticides in the second canister after the 24 hour run. The increase in quantity did not appear to be as predictable as the migration from the filter to the primary canister.

There is, therefore, a migration and desorption pattern throughout the system. The magnitude of the migration appears to depend on the characteristics of each pesticide. Desorption of the pesticides appears to take place from the primary canister to the secondary canister.

TABLE 11

Migration of Various Pesticides Through the Pesticide Collection Module-Vapor Phase Pesticides

Pesticide	Quantity of Test Pesticide Injected, ng	Quantity of Pesticide in Module Component, ng						Quantity of Pesticide Not Accounted For	
		Filter		Primary Canister		Secondary Canister			
		1 Hour	24 Hours	1 Hour	24 Hours	1 Hour	24 Hours	1 Hour	24 Hours
p,p'-DDD	5180	1889	0	2332	3914	374	815	585	451
Percent	(100.0)	(36.5)	(0.0)	(45.0)	(75.6)	(7.2)	(15.7)	(11.3)	(8.7)
o,p'-DDT	6840	1446	0	3587	5114	228	828	1579	898
Percent	(100.0)	(21.1)	(0.0)	(52.4)	(74.8)	(3.3)	(12.1)	(23.2)	(13.1)
Methyl Parathion	5280	419	0	2367	2719	626	675	2868	2886
Percent	(100.0)	(7.9)	(0.0)	(44.8)	(51.5)	(11.8)	(12.8)	(35.5)	(35.7)
Parathion	8840	5824	0	2643	7793	217	2065	156	0
Percent	(100.0)	(65.9)	(0.0)	(29.9)	(88.2)	(2.4)	(23.4)	(4.2)	(0.0)

SECTION X

CALCULATION OF PESTICIDE CONCENTRATIONS IN COLLECTED FIELD SAMPLES

The quantity of each pesticide found in the gas chromatographic analysis of the sample eluates was calculated on the basis of each compound present in the volume of air sampled. The total weight in nanograms of each pesticide was calculated from the formula:

(1) $$\text{Nanograms Pesticide present in the volume of air sampled} = \frac{\text{Nanograms Pesticide}}{\mu\text{l of eluate injected}} \times F_1 \times F_2 \times V$$

where Nanograms Pesticide = Nanograms of each pesticide determined by gas chromatographic analysis

F_1 = Normalizing factor to correct for analytical recovery efficiency

F_2 = Normalization factor to correct for sampling system efficiency

V = Volume of final eluate concentrate, in ml.

F_1 for the study pesticides has been given in Table 8, Section VII. F_2, determined for each pesticide, has been given in Table 10, Section IX. V was either 10 ml or 1 ml, depending on the pesticide to be determined.

The calculation of the concentration of airborne pesticides in the collected air samples was done according to the formula:

$$(2)\quad \text{Nanograms/cubic meter} = t \times \frac{\text{Nanograms Pesticide in Air Sample}}{\text{A.F.} \times \text{P.C.F.} \times 0.02832}$$

where t = Time of sampling in minutes

A.F. = Average flow, sampling rate in cubic feet per minute (CFM), calculated by

$$\frac{\text{Flow A} + \text{Flow B}}{2}$$

P.C.F. = Pressure (altitude) correction factor

0.02832 = Conversion factor for converting cubic feet to cubic meters

Flows A and B are flowmeter readings taken before and at the end of sampling. Flow A is automatically set at 10 CFM at the beginning of each sampling period. Since the flow of air through the pesticide collection module changes slightly as the particulate layer builds on the glass fiber filter mat, the flow is rechecked at the time the sampler is replaced.

A pressure correction factor, P.C.F., was assumed for each station location based on the altitude above sea level of the surrounding goegraphical area. By referring to a table of barometric pressure at various altitudes (9), a pressure correction factor may be calculated for each site. The pressure correction factors for the study sampling

locations is shown in Table 12. No similar temperature correction factor was applied since no adequate temperature value can be assumed for each location.

Since the volume of data collected during the course of the study was quite large, and the calculations tedious and time consuming, a computer program was written in Fortran IV in order to calculate and tabulate the data in a convenient and usable form. A copy of the complete program is given in Appendix G. The program was written to calculate Equation 2 only. A copy of the internal pesticide coding form for the raw data is shown in Table 13.

The computer system used was a Xerox Data System XDS Sigma 5.

TABLE 12

Atmospheric Pressure Correction

Factors for Pesticides Sampling Site

LOCATION	ELEVATION ABOVE SEA LEVEL, FT.	PRESSURE CORRECTION FACTOR
Winter Haven, Florida	25	0.998
Buffalo, New York	575	0.979
Rome, New York	435	0.983
Jordan, New York	390	0.985
Lafayette, New York	1250	0.954
Naples, New York	818	0.970
Syracuse, New York	400	0.985
Lubbock, Texas	3243	0.887

TABLE 13

Pesticide Coding Form

Code	Station Code	Date	Sampling Time, Min.	Flow Start, cfm	Flow Stop, cfm	Pressure Correction Factor	Tare Weight, grams	Gross Weight, grams
5								
1	2 – 9	10 – 15	16 – 19	20 – 22	23 – 25	26 – 29	30 – 34	35 – 39

Pesticide Names	columns	Pesticide Codes 1 – 5	Weight Nanograms 9 – 13
Aldrin		5 1 1 0 1	
DDD		5 1 1 0 6	
DDT		5 1 1 0 7	
Heptachlor		5 1 1 0 9	
DDE		5 1 1 1 8	
Endrin		5 1 2 0 4	
Heptachlor epoxide		5 1 2 0 8	
Malathion		5 1 3 1 1	
Methyl Parathion		5 1 4 1 9	
Parathion		5 1 4 2 1	
Total 2,4-D		5 4 1 3 2	

SECTION XI

RESULTS OF AIRBORNE PESTICIDE SAMPLING

Estimated Detection Limits of Airborne Pesticides

The estimated limit of detection for each study pesticide was calculated from the minimum detectable quantities determined by either electron capture detection or flame photometric detection as shown in Tables 2 and 3, Appendix F.

The minimum detectable quantity was defined as that quantity of each test pesticide which gave a 10% full scale deflection on a strip chart recorder with a 0-1 mv full scale range and a noise level of 1%. The estimated detection limit of airborne pesticides, in nanograms per cubic meter was calculated by the formula:

$$\text{Estimated Detection Limit} = \frac{(\text{M.D.Q.})(\text{V.C.})}{(\text{I.V.})(\text{A.V.S.})}$$

where

M.D.Q. = minimum detectable quantity of pesticide

V.C. = volume of concentrated eluate from the separation and cleanup procedure

I.V. = injection volume chromatographed

A.V.S. = volume of air sampled

The injection volume was maintained at 5 µl, and the volume of air sampled during a 24 hour sampling period was 403 cubic meters. The volume of the eluate concentrate was 10 ml for the 6% ethyl ether in petroleum ether and total 2,4-D methyl ester eluates for electron capture detection gas chromatography. The 50% ethyl ether in petroleum ether eluates were concentrated to 10 ml for electron capture detection, and further reduced to 1 ml for flame photometric detection of the organophosphorus pesticides. The calculated estimated detection limit for each of the test pesticides is given in Table 14.

The values calculated for the minimum detectable limit, however, may be misleading since they are calculated for ideal gas chromatographic operating conditions, that is, the input and output attenuation settings are set so that the background noise level and recorder drift will not exceed 1%, dependent on the electrometer and detector system used. As a result, an identifiable peak may result which is less than 10% full scale deflection, as in the case of flame photometric detection, from injections of the 6% or 50% ethyl ether in petroleum ether eluates at the maximum sensitivity settings of the gas chromatograph.

In most instances the use of the maximum sensitivity settings for electron capture is not practical, primarily due to the nonspecificity of the detection technique. The chromatograms resulting from the injection of the 6% and 50% eluate are, in general, more complex due to

Table 14

Estimated Detection Limits of Airborne Pesticides,
Nanograms/Cubic Meter*

Pesticide	Estimated Detection Limit, Ng/Cubic Meter
Aldrin	0.04
o,p'-DDD	0.12
p,p'-DDD	0.08
o,p'-DDE	0.15
p,p'-DDE	0.13
o,p'-DDT	0.10
p,p'-DDT	0.27
Endrin	0.29
Heptachlor	0.03
Heptachlor epoxide	0.07
Malathion**	0.09
Methyl Parathion**	0.04
Parathion**	0.05
2,4-D Methyl Ester	0.30

*Electron Capture Detection
**Flame Photometric Detection

the collection of quantities of compounds present in the ambient atmosphere which are carried through the separation and cleanup procedures. In order to reduce the background to a practical, usable level, adjustment of the output attenuation to a less sensitive setting is necessary, thereby, in effect, increasing the minimum limit of detection.

Concentration of Airborne Pesticides in the Field Samples

During the course of the field study, 202 samples were analyzed for the study pesticides listed in Section III. The results of the analyses are given in Tables 15 through 22 for Winter Haven, Florida, Buffalo, Rome, Jordan, Lafayette, Naples, and Syracuse, New York, and Lubbock, Texas, respectively.

Pesticides were found on 17 sampling days of the 26 possible (65.4%). The concentration range of each pesticide found at each sampling location is shown in Table 23. The overall concentration ranges, in nanograms per cubic meter, were aldrin, 0.22-2.15; DDE, 0.14-2.16; DDT, 0.54-1101; heptachlor, 0.09-1.32; malathion, 0.06-3.53; methyl parathion, 0.02-0.84; parathion, 0.03-1.42; and total 2,4-D acid, 1.15-1.54.

No DDD, endrin, or heptachlor epoxide were detected in any sample from any sampling site.

A summary of the occurrences of airborne pesticides by station are given in Table 24. Pesticides were found at each station during the sampling year. The number of sampling dates pesticides were found at

Table 15

AIRBORNE PESTICIDE DATA
VALUE BY DATE
NG/CM

STATION CODE: 10488001
STATION NAME: Winter Haven, Fla.

Date	Aldrin	DDD	DDT	Hepta-clor	DDE	Endrin	Hepta-clor Epoxide	Mala-thion	Methyl Para-thion	Para-thion	Total 2,4-D	Susp. Part. Matter
70/12/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	70.0
70/12/14	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	44.1
71/01/07	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	34.6
71/01/13	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	14.7
71/02/02	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	34.3
71/02/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.0
71/02/27	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	48.2
71/03/08	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.0
71/03/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	34.2
71/04/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	20.6
71/04/21	.00	.00	2.03	.00	.37	.00	.00	.35	.00	.00	.00	132.1
71/05/04	.00	.00	5.24	.00	.74	.00	.00	1.30	.00	.00	.00	62.9
71/05/21	.00	.00	.00	.00	.00	.00	.00	3.53	.00	.00	.00	64.9
71/06/05	.00	.00	3.44	.00	1.94	.00	.00	.11	.00	.00	.00	24.2
71/06/14	.00	.00	5.22	.00	.93	.00	.00	.18	.00	.00	.00	47.6
71/07/03	.00	.00	.00	.00	.00	.00	.00	2.03	.00	.00	.00	34.4
71/07/16	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	37.6
71/07/26	.00	.00	.00	.00	.00	.00	.00	.20	.00	.00	.00	42.8
71/08/08	.00	.00	.00	.00	.00	.00	.00	.51	.00	.00	.00	31.7
71/08/25	.00	.00	.00	.09	.53	.00	.00	.00	.00	.58	.00	27.0
71/09/11	1.73	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	64.5
71/09/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.41	.00	37.8
71/10/06	.00	.00	3.29	.61	.27	.00	.00	.00	.04	.07	.00	29.7
71/10/23	1.04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	28.5
71/11/04	.00	.00	.00	1.32	.00	.00	.00	.00	.00	.00	.00	45.6
71/11/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	31.9

Table 16

AIRBORNE PESTICIDE DATA
VALUE BY DATE
NG/CM

STATION CODE: 33066001
STATION NAME: Buffalo, N. Y.

Date	Aldrin	DDD	DDT	Hepta-clor	DDE	Endrin	Hepta-clor Epoxide	Mala-thion	Methyl Para-thion	Para-thion	Total 2,4-D	Susp. Part. Matter
70/12/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	84.3
70/12/14	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	40.9
71/01/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	97.5
71/01/13	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	34.1
71/01/29	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	711.9
71/02/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	84.3
71/02/27	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	68.3
71/03/08	.00	.00	.00	.00	.00	.00	.00	.43	.00	.06	.00	51.1
71/03/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	60.6
71/04/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	42.8
71/04/21	.00	.00	.00	.00	.00	.00	.00	.32	.31	.35	.00	109.2
71/05/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	89.1
71/05/21	.22	.00	1.74	.00	.37	.00	.00	.00	.00	.00	.00	171.1
71/06/05	.00	.00	1101.38	.00	.00	.00	.00	.39	.00	.00	.00	74.1
71/06/14	.33	.00	3.71	.00	.00	.00	.00	.40	.00	.00	.00	71.1
71/07/01	.00	.00	3.03	.00	.00	.00	.00	.07	.00	.00	.00	82.6
71/07/16	.00	.00	.00	.00	.00	.00	.00	.55	.00	1.42	.00	71.1
71/07/26	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	99.4
71/08/08	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	72.1
71/08/25	.00	.00	.00	.00	.00	.00	.00	.00	.00	.03	.00	85.9
71/09/11	1.95	.00	.00	.00	.00	.00	.00	1.81	.00	.04	.00	280.0
71/09/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	79.4
71/10/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	41.3
71/10/23	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	50.4
71/11/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	68.4
71/11/17	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	112.5

Table 17

AIRBORNE PESTICIDE DATA
VALUE BY DATE
NG/CM

STATION CODE: 33506001
STATION NAME: Rome, N. Y.

Date	Aldrin	DDD	DDT	Hepta-clor	DDE	Endrin	Hepta-clor Epoxide	Mala-thion	Methyl Para-thion	Para-thion	Total 2,4-D	Susp. Part. Matter
70/12/12	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	22.5
70/12/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	20.7
71/01/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	21.7
71/01/13	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	7.0
71/01/29	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	25.0
71/02/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	53.5
71/02/27	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	30.9
71/03/08	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	16.5
71/03/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	10.5
71/04/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	28.9
71/04/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	29.4
71/05/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	14.5
71/05/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	47.4
71/06/05	.00	.00	1.08	.00	.00	.00	.00	.00	.00	.00	.00	22.5
71/06/14	.45	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	43.2
71/07/01	.00	.00	.00	.00	.00	.00	.00	.08	.00	.00	.00	46.4
71/07/16	.28	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	40.2
71/07/26	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	40.4
71/08/08	.00	.00	.00	.00	.00	.00	.00	.00	.03	.00	.00	39.2
71/08/25	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	43.4
71/09/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	1.54	46.0
71/09/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	21.5
71/10/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	26.2
71/10/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	30.4
71/11/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	13.0
71/11/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	25.9

Table 18

AIRBORNE PESTICIDE DATA
VALUE BY DATE
NG/CM

STATION CODE: 33510001
STATION NAME: Jordan, N. Y.

Date	Aldrin	DDD	DDT	Hepta-clor	DDE	Endrin	Hepta-clor Epoxide	Mala-thion	Methyl Para-thion	Para-thion	Total 2,4-D	Susp. Part. Matter
70/12/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	221.6
70/12/14	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	75.4
71/01/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	17.2
71/01/13	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	154.7
71/01/29	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.0
71/02/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	67.0
71/03/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	85.7
71/03/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	79.1
71/03/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	10.3
71/04/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	52.5
71/04/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	28.3
71/05/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	35.1
71/05/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	49.5
71/06/05	.00	.00	.00	.00	.00	.00	.00	.22	.00	.00	.00	45.8
71/06/14	.00	.00	.00	.00	.00	.00	.00	.19	.00	.00	.00	59.1
71/07/01	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	46.8
71/07/16	2.15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	30.8
71/07/26	.00	.00	.00	.00	.00	.00	.00	.08	.00	.21	.00	46.9
71/08/08	.00	.00	.00	.00	.00	.00	.00	.00	.00	.24	.00	48.3
71/08/25	.00	.00	1.22	.00	.14	.00	.00	.00	.00	.12	.00	43.9
71/09/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.27	1.15	51.0
71/09/21	.00	.00	1.64	.00	.00	.00	.00	.00	.00	.00	.00	84.8
71/10/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	26.2
71/10/23	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	48.3
71/11/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	33.3
71/11/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	44.6

Table 19

AIRBORNE PESTICIDE DATA
VALUE BY DATE
NG/CM

STATION CODE: 33510002
STATION NAME: Lafayette, N. Y.

Date	Aldrin	DDD	DDT	Hepta-clor	DDE	Endrin	Hepta-clor Epoxide	Mala-thion	Methyl Para-thion	Para-thion	Total 2,4-D	Susp. Part. Matter
70/12/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	25.1
70/12/14	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	85.1
71/01/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	26.7
71/01/13	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	10.9
71/01/25	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.0
71/02/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	35.8
71/02/27	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.0
71/03/08	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	22.9
71/03/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	38.6
71/04/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	52.4
71/04/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	38.3
71/05/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	32.1
71/05/21	.00	.00	.00	.00	.00	.00	.00	.12	.05	.00	.00	55.8
71/06/05	.00	.00	2.18	.00	1.11	.00	.00	.00	.00	.00	.00	42.4
71/06/14	.00	.00	7.65	.00	.15	.00	.00	.00	.00	.00	.00	56.0
71/07/01	.00	.00	4.84	.00	1.10	.00	.00	.12	.00	.00	.00	41.4
71/07/16	.00	.00	1.32	.00	.84	.00	.00	.00	.00	.00	.00	37.0
71/07/26	.00	.00	2.89	.00	1.45	.00	.00	.00	.00	.00	.00	55.5
71/08/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	48.6
71/08/25	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	49.9
71/09/11	.00	.00	2.58	.00	1.52	.00	.00	.00	.00	.24	.00	48.2
71/09/21	.00	.00	1.24	.00	.55	.00	.00	.00	.00	.00	.00	33.2
71/10/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	21.8
71/10/23	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	91.2
71/11/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	22.0
71/11/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	75.1

Table 20

AIRBORNE PESTICIDE DATA
VALUE BY DATE
NG/CM

STATION CODE: 33512001
STATION NAME: Naples, N. Y.

Date	Aldrin	DDD	DDT	Hepta-clor	DDE	Endrin	Hepta-clor Epoxide	Mala-thion	Methyl Para-thion	Para-thion	Total 2,4-D	Susp. Part. Matter
70/12/12	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	56.9
70/12/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	60.9
71/01/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	4.2
71/01/13	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	29.8
71/02/29	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	25.3
71/02/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	38.4
71/02/27	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	27.3
71/03/08	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	20.5
71/03/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	15.9
71/04/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	25.8
71/04/21	.00	.00	.00	.00	.00	.00	.00	.14	.08	.13	.00	102.9
71/05/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00		43.0
71/05/27	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	42.5
71/06/05	.00	.00	2.07	.00	.73	.00	.00	.17	.00	.00	.00	65.5
71/06/14	.00	.00	.00	.00	.00	.00	.00	.06	.00	.00	.00	46.8
71/07/01	.00	.00	7.71	.00	2.16	.00	.00	.00	.00	.00	.00	40.2
71/07/16	.00	.00	3.08	.00	.63	.00	.00	.00	.00	.00	.00	44.8
71/07/26	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	34.6
71/05/08	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	65.4
71/05/25	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	42.5
71/09/13	.00	.00	1.82	.00	.55	.00	.00	.00	.00	.35	.00	12.6
71/09/23	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	49.0
71/10/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	16.9
71/10/24	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	27.0
71/11/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	154.5
71/11/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	21.5

Table 21

AIRBORNE PESTICIDE DATA
VALUE BY DATE
NG/CM

STATION CODE: 33662001
STATION NAME: Syracuse, N. Y.

Date	Aldrin	DDD	DDT	Hepta-clor	DDE	Endrin	Hepta-clor Epoxide	Mala-thion	Methyl Para-thion	Para-thion	Total 2,4-D	Susp. Part. Matter
70/12/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	83.8
70/12/14	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	108.3
71/01/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	96.3
71/01/13	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	172.3
71/01/29	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.0
71/02/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	55.2
71/03/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	101.1
71/03/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	100.8
71/03/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	123.8
71/04/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	123.4
71/04/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	92.8
71/05/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	181.9
71/05/21	.00	.00	1.24	.00	.38	.00	.00	.00	.00	.00	.00	125.4
71/06/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	64.6
71/06/14	.00	.00	384.04	.00	.00	.00	.00	.10	.00	.00	.00	67.5
71/07/01	.00	.00	.00	.00	.00	.00	.00	.11	.00	.00	.00	70.4
71/07/16	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	127.2
71/07/26	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	94.7
71/08/08	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	88.8
71/08/25	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	143.0
71/09/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	92.8
71/09/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	22.6
71/10/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	61.1
71/10/23	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	48.8
71/11/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	62.5
71/11/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	190.2

Table 22

AIRBORNE PESTICIDE DATA
VALUE BY DATE
NG/CM

STATION CODE: 45334001
STATION NAME: Lubbock, Texas

Date	Aldrin	DDD	DDT	Hepta-clor	DDE	Endrin	Hepta-clor Epoxide	Mala-thion	Methyl Para-thion	Para-thion	Total 2,4-D	Susp. Part. Matter
70/12/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.0
70/12/14	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.0
71/01/05	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	36.3
71/01/13	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	119.6
71/01/29	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	150.4
71/02/11	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	178.9
71/02/27	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	47.3
71/03/08	.00	.00	.00	.00	.00	.00	.00	.61	.00	.16	.00	74.6
71/03/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	76.3
71/04/04	.00	.00	5.78	.00	.00	.00	.00	.06	.11	.08	.00	59.0
71/04/21	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	94.7
71/05/04	.00	.00	.54	.00	.00	.00	.00	.08	.00	.00	.00	298.9
71/05/21	.00	.00	.54	.00	.31	.00	.00	.00	.00	.00	.00	93.9
71/06/05	.00	.00	.00	.00	1.22	.00	.00	.28	.00	.00	.00	163.9
71/06/14	.00	.00	345.37	.00	.97	.00	.00	.06	.00	.00	.00	115.6
71/07/01	.00	.00	2.68	.00	1.07	.00	.00	.37	.00	.13	.00	110.9
71/07/16	.00	.00	1.26	.00	.43	.00	.00	.00	.00	.00	.00	89.9
71/07/26	.00	.00	.00	.00	.00	.00	.00	.00	.00	.10	.00	71.3
71/08/08	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	54.7
71/08/25	.00	.00	3.38	.00	1.36	.00	.00	.00	.00	1.03	.00	53.1
71/09/15	.00	.00	.00	.00	.00	.00	.00	.00	.84	.13	.00	568.6
71/09/22	.00	.00	.00	.00	.84	.00	.00	.00	.02	.07	.00	20.3
71/10/06	.00	.00	.00	.00	.00	.00	.00	.00	.00	.15	.00	74.3
71/10/23	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	39.7
71/11/04	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	51.3
71/11/15	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	78.2

TABLE 23

Concentration Ranges of Test Pesticides in Collected Field Samples

Pesticide	Concentration Range, Nanograms/Cubic Meter								
	Winter Haven, Fla.	Buffalo, N.Y.	Rome, N.Y.	Jordan, N.Y.	Lafayette, N.Y.	Naples, N.Y.	Syracuse, N.Y.	Lubbock, Texas	Range, All Stations
Aldrin	1.04-1.08	0.22-1.96	--	2.15	--	--	--	--	0.22-2.15
DDE	0.27-1.94	0.37	--	0.14	0.15-1.52	0.63-2.16	0.38	0.31-1.36	0.14-2.16
DDT	2.03-5.24	1.74-1101	1.08	1.22-1.64	1.24-7.65	1.82-7.71	1.24-384	0.54-345	0.54-1101
Heptachlor	0.09-1.32	--	--	--	--	--	--	--	0.09-1.32
Malathion	0.11-3.53	0.07-1.81	0.06	0.08-0.22	0.12	0.06-0.17	0.10-0.11	0.06-0.61	0.06-3.53
Methyl Parathion	0.04	0.31	0.03	--	0.05	0.05	--	0.02-0.84	0.02-0.84
Parathion	0.07-0.58	0.03-1.42	--	0.12-0.27	0.24	0.13-0.35	--	0.07-1.03	0.03-1.42
Total 2,4-D	--	--	1.54	1.15	--	--	--	--	1.15-1.54

TABLE 24

Occurrence of Airborne Pesticides -- December, 1970 - November, 1971

Pesticide	Number of Occurrences by Station							
	Winter Haven, Fla.	Buffalo, N.Y.	Rome, N.Y.	Jordan, N.Y.	Lafayette, N.Y.	Naples, N.Y.	Syracuse, N.Y.	Lubbock Texas
Aldrin	2	3	2	1	0	0	0	0
DDD	0	0	0	0	0	0	0	0
DDE	6	1	0	1	7	4	1	7
DDT	5	4	1	2	7	4	2	7
Endrin	0	0	0	0	0	0	0	0
Heptachlor	3	0	0	0	0	0	0	0
Heptachlor Epoxide	0	0	0	0	0	0	0	0
Malathion	8	7	1	3	2	3	2	5
Methyl Parathion	1	1	1	0	1	1	0	3
Parathion	3	5	0	4	1	2	0	8
Total 2,4-D	0	0	1	1	0	0	0	0
No. Sampling Dates Pesticides Found	14	10	6	8	8	6	3	13
% of Total Sampling Dates	53.8	38.5	23.1	30.8	30.8	23.1	11.5	50

each sampling site were 14 (53.8%) at Winter Haven, Florida; 10 (38.5%) at Buffalo; 6 (23.1%) at Rome; 8 (30.8%) at Jordan; 8 (30.8%) at Lafayette; 6 (23.1%) at Naples; 3 (11.5%) at Syracuse; and 13 (50%) at Lubbock, Texas.

The data presented does not separate the isomers of DDE and DDT into the o,p´ or p,p´ isomers of each. The data for DDE represents p,p´-DDE only, since o,p´-DDE was not detected in any sample. Table 25 lists the o,p´-DDT and p,p´-DDT data, as well as the ratio of o,p´-DDT to p,p´-DDT found in samples where DDT was found. The primary isomer is p,p´-DDT. The quantity of o,p´-DDT varied widely from sample to sample so that the ratio of o,p´-DDT to p,p´-DDT was not consistent. Commercial preparation of DDT may contain as much as 20% o,p´-DDT. Therefore, an o,p´/p,p´ ratio of greater than 0.20 might indicate the presence of a compound which may be misinterpreted as o,p´-DDT. Whether these peaks are actually o,p´-DDT, a similarly behaving compound, or a combination of the two is open to speculation at this point.

TABLE 25

Total Quantitv of o,p´-DDT and p,p´-DDT in Collected Field Samples

Sampling Location and Date	Quantity, ng o,p´-DDT	Quantity, ng p,p´-DDT	Ratio, o,p´/p,p´
Winter Haven, Florida			
4-21-71	108	696	0.16
5-04-71	222	1911	0.12
6-05-71	---	1366	0
6-14-71	265	1531	0.17
10-06-71	355	982	0.36
Buffalo, New York			
5-21-71	70	625	0.11
6-05-71	22765	20768	1.10
6-14-71	489	975	0.50
7-01-71	---	1208	0
Rome, New York			
6-05-71	---	432	0
Jordan, New York			
8-25-71	---	498	0
9-21-71	---	675	0
Lafayette, New York			
6-05-71	164	700	0.23
6-14-71	462	2107	0.22
7-01-71	512	1370	0.37
7-16-71	111	402	0.28
7-26-71	352	773	0.46
9-11-71	614	1044	0.59
9-21-71	---	482	0

TABLE 25 (Cont'd)

Total Quantity of o,p´-DDT and p,p´-DDT in Collected Field Samples

Sampling Location and Date	Quantity, ng		Ratio,
	o,p´-DDT	p,p´-DDT	o,p´/p,p´
Naples, New York			
6-05-71]	38	783	0.05
7-01-71	1134	1610	0.70
7-16-71	129	1091	0.12
9-13-71	---	722	0
Syracuse, New York			
5-21-71	75	416	0.18
6-14-71	6755	8440	0.80
Lubbock, Texas			
3-21-71	65	383	0.17
4-04-71	172	1652	0.10
5-04-71	---	181	0
5-21-71	19	176	0.11
6-05-71	4111	4997	0.82
6-14-71	4416	7951	0.56
7-01-71	86	872	0.10
7-16-71	78	385	0.20
8-25-71	398	844	0.47

SECTION XII

DISCUSSION OF THE EXPERIMENTAL AIRBORNE PESTICIDE NETWORK AND RESULTS OF SAMPLING

Evaluation of the Field Sampling Method of Collection of Airborne Pesticides

Sampling was conducted for twelve months, from December, 1970 through November, 1971. During this period there were 26 scheduled sampling dates. As a result, the potential number of samples for the twelve month period was 208. The data listed in Table 26 summarizes the overall operation of the network. Of the possible 208 samples, 176 were collected on the scheduled date; 26 were collected within the specified sampling period, and six samples were missed completely. Table 27 lists the occurrence of missing samples and the number of reported timing errors by station. Four of the six samples lost were due to blizzard conditions in the Syracuse, New York area.

The data indicate a sample loss rate of 2.8% in the field due to various circumstances. Timing errors occurred in 1.4% of the samples, resulting in a deviation from the required 24 hours sampling period. The combined deviations from the sampling schedule were 4.2%. The collection of 97.2% of the scheduled samples indicates that the instrument, when properly serviced and with a minimum of attention and maintenance, is highly reliable under varying environmental conditions.

TABLE 26

Summary of Network Operation

	Scheduled Sample Date	Number of Samples on Date	Number Samples Within Time Period	Samples Missing	Remarks
1	12/5/70	7	1	-	Timer - one 10 day run
2	12/14/70	6	2	-	-
3	1/5/71	6	2	-	1 filter mat damaged
4	1/13/71	8	-	-	-
5	1/29/71	4	1	3	3 lost due to blizzard-filter mat damaged
6	2/11/71	7	-	1	shipping error
7	2/27/71	5	2	1	instrument did not run properly
8	3/8/71	5	2	1	shipping error
9	3/21/71	8	-	-	-
10	4/4/71	7	1	-	-
11	4/21/71	8	-	-	one 34-hr. sample
12	5/4/71	8	-	-	
13	5/21/71	8	-	-	
14	6/5/71	8	-	-	
15	6/14/71	8	-	-	
16	7/1/71	6	2	-	
17	7/16/71	8	-	-	
18	7/26/71	8	-	-	
19	8/8/71	6	2	-	
20	8/25/71	7	1	-	
21	9/11/71	6	2	-	
22	9/21/71	5	3	-	1 sample ran for two 24 hr periods
23	10/6/71	8	-	-	1 data sheet missing
24	10/23/71	6	2	-	
25	11/4/71	7	1	-	
26	11/15/71	6	2	-	1 data sheet missing
	Total	176	26	6	

TABLE 27

Station Operation by Location -- General Source of Problems

Station	Number of Times Sample Missing	Reason Sample Missed	Timing Errors
Winter Haven	2	shipping error	-
Buffalo	0	-	-
Rome	0	-	-
Jordan	1	lost due to blizzard	1 sample ran 10 consecutive days 1 sample ran 2 24-hr. periods
Lafayette	2	lost due to blizzard	-
Naples	0	-	-
Syracuse	1	lost due to blizzard	
Lubbock	0	-	1 sample ran 34 hr.
TOTAL	6		

Changes in Viscosity of the Cottonseed Oil-Coated Glass Beads

An observation was made during the course of operation of the network concerning the physical appearance of the cottonseed oil coated glass beads after sampling had occurred.

The cottonseed oil used to coat the beads came from a common stock of refined oil, and did not vary in appearance during the course of the study. Preparation and assembly of the pesticide collection modules were done in the same laboratory under constant environmental conditions.

However, 40 samples were received in which the beads appeared to be gummed together in a more viscous mass than was considered normal. Gumming occurred in 19.8% of the samples collected (Table 28).

The occurrence of gumming did not appear to be periodic in nature, but occurred randomly at each sampling location. Simultaneous occurrence of gumming and pesticides occurred in 18 instances, also on a random basis. The Lafayette, N.Y. station showed the highest number of incidences of gumming (ten) of all the sampling stations.

The cause of the gumming is open to some speculation at this point. Since cottonseed oil is a relatively slow drying oil, it may be possible that some polymerization may have taken place due to interaction with airborne oxidants or other reactive material. The possibility exists that some

TABLE 28

Occurrence of Cottonseed-Oil Gumming During Network Operation

Date of Occurrence	Winter Haven, Fla.	Buffalo, N.Y.	Rome, N.Y.	Jordan, N.Y.	Lafayette, N.Y.	Naples, N.Y.	Syracuse, N.Y.	Lubbock, Texas
1-5-71			C*	G	G	G	G	G
1-6-71		G						
1-7-71	G							
1-29-71						G		
2-2-71	G							
2-11-71				G	G		G	
3-6-71				G				
5-4-71					G			
5-21-71	(G)				(G)			(G)
6-5-71			(G)		(G)		(G)	
6-14-71				(G)				
7-10-71			(G)		(G)			
7-26-71	(G)	(G)	G	(G)	(G)		G	(G)
8-8-71	(G)	G		(G)			G	
8-25-71		(G)			G			
9-13-71						G		
10-6-71					G			
10-23-71	(G)							
11-4-71					G			
No. of Sampling Dates Gumming Found	6	4	4	6	10	3	5	2
No. of Simultaneous Occurrence of Pesticides & Gumming	4	3	2	3	4	0		

NOTE: G -- Occurrence of gumming.
(G) -- Occurrence of both gumming and pesticide.

materials which are absorbed react with the oil, or possibly cause some degradation. It may also be possible that enough airborne gases may be trapped, thereby causing an increased viscosity of the collection medium.

In any respect, the primary difficulty which the increased viscosity causes is the enhancement of emulsion formation during acetonitrile partitioning, with subsequent waiting periods while the emulsion breaks. It is not known at this point whether the increased viscosity of the cottonseed oil coated glass bead collection media has any affect on the overall collection efficiency of the system.

Results of Airborne Pesticide Sampling

The scheduled operation of the network resulted in the collection of 202 samples. Analysis of the samples showed that, of the 202 samples collected, identifiable pesticides were found in 68 samples (33.5%).

The number of incidences of the test pesticides occurring in these samples, in decreasing number of occurrences are DDT, 32; malathion, 31, DDE, 27; parathion, 23; methyl parathion, 8; heptachlor, 3; and total 2,4-D acids, 2. No detectable quantities of DDD, endrin, or heptachlor epoxide were found.

The primary isomer of DDT found was the p,p′ isomer. The quantity of o,p′-DDT varied considerably from sample to sample so that there was no consistent ratio of o,p′-DDT to p,p′-DDT. The data for DDE represents entirely p,p′-DDE since no o,p′-DDE was found in detectable quantities.

Observation of the data does indicate a seasonal trend in the appearance of the pesticides at each station. This is clearly indicated by the appearance of pesticides in Winter Haven, Florida, and Lubbock, Texas samples beginning in March, 1971, and ending in October. With the exception of one sample in early March, 1971 in Buffalo, detection of pesticides in New York State began in late April and May, 1971 and lasted through September.

Inspection of the pesticide concentration data and the suspended particulate matter data collected for each sample shows that there is no apparent correlation between the two. This observation, however, does not mean that there were no pesticides adsorbed on the surface of the suspended particulate matter collected, but that when the glass fiber filter mat and cottonseed oil-coated glass beads are analyzed together, differentiation between adsorbed pesticides on the filter and those trapped in the cottonseed oil is not possible.

Pesticide field monitoring data for each location and sampling date is given in Appendix I.

SECTION XIII

DETECTION OF PESTICIDES OTHER THAN STUDY COMPOUNDS

Gas chromatographic analysis of the eluates obtained in this study showed very complex chromatograms for the 6% and 50% eluates, indicating the retention of a wide range of airborne constituents by the collection module.

Identification of the extraneous peaks is a difficult task due to the wide variety of pesticides used, plus the tremendous quantities of other organic compounds which may be collected and carried simultaneously through the separation and cleanup procedure with the pesticides of interest. An example of this type of compound is polychlorinated biphenyls (PCB's).

One pesticide, however, had been collected in a sufficient quantity to be confirmed. Ethion, an organophosphorus pesticide, was found in the 6% eluate from the Florisil column cleanup for nine consecutive samples from the Winter Haven, Florida collection station.

The results of the analysis are shown in Table 29. The concentrations were estimated on the basis of 100% collection efficiency for ethion, as well as 100% analytical scheme recovery. The values listed, then, are very conservative estimates of the concentration of ethion in the ambient atmosphere at the time of sampling.

TABLE 29

Occurrence of Ethion in Winter Haven, Florida Samples (6% Eluate)

Date of Occurrence	Ethion, Estimated Nanograms/Cubic Meter
7-3-71	39,600
7-16-71	66,700
7-26-71	1,940
8-8-71	560
8-26-71	1,250
9-11-71	1,300
9-21-71	2,660
10-6-71	620
10-23-71	Trace

An examination of the table shows high concentrations of ethion in every sample collected from July through October, 1971. Only in the October 23 sample did the concentration reach a trace level, that is, the response of the flame photometric detector to a 5 µl injection of a 10 ml 6% eluate concentrate was less than 10% full scale response to the recorder at the most sensitive instrument settings.

The concentration of airborne ethion ranged from trace quantities to up to 66,700 ng/cubic meter.

SECTION XIV

COLD STORAGE STABILITY TESTS

A series of tests were designed to determine if changes in test pesticide quantities would occur if the collected field samples were stored at low temperatures for a period of time prior to analysis.

A series of four sets, four replicates per set, of cottonseed oil coated glass beads were prepared by adding 3 ml of cottonseed oil to a glass container containing 140 ml of 3 mm Pyrex glass beads and agitated until the beads were thoroughly coated. Then the coated glass beads were spiked with pesticide standards in hexane.

One series of containers were analyzed immediately. The remaining three were stored for periods of one, three and five months, respectively, at 3°C.

The results of the storage test are shown in Table 30. This set of data indicate that there is little change in the quantity of pesticide during cold storage for a time period of up to 5 months.

During the course of the project, storing the samples in the collection module was not practical from an equipment and space standpoint, so the collected samples were carried through the extraction procedure as outlined in Appendix E, and the hexane extracts stored in

TABLE 30

Cold Storage Stability Tests Summary of Average

Percent of Pesticides Recovered

Pesticide	Quantity Added, ng	Months Stored, 0	1	3	5
Aldrin	2000	82.3	76.4	84.7	61.3
o,p´-DDD	5000	101.1	123.0	93.6	130.8
p,p´-DDD	5000	106.4	107.9	118.0	81.4*
o,p´-DDT	5000	110.1	101.8	92.4	91.8
p,p´-DDT	5000	104.4	117.6	86.3	96.2
Endrin	1000	-**	91.5	94.2	94.6
Heptachlor	2000	89.1	83.9	93.1	83.2
Heptachlor Epoxide	5000	88.9	112.0	131.0	125.8
Malathion	10,000	112.0	89.1	105.8	100.0
Methyl Parathion	2000	123.2	65.8	76.3	84.2
Parathion	2000	111.2	76.4	82.1	90.4

*Only one value
**Samples lost

a refrigerator until analysis could be performed. The cold storage stability tests should be repeated to cover potential changes in quantities of pesticides in the hexane extracts with time. Based on the data presented in this section, little change with time would be expected.

SECTION XV

SELECTION OF LIQUID COATINGS FOR GLASS BEAD ABSORBING MEDIA

The selection of a material to be used as a liquid coating for the glass bead collection media in the pesticide collection module is extremely important. The following selection criteria, in increasing order of importance are:

1. Proper viscosity to coat the glass beads.
2. Will not evaporate after 48 hours of operation.
3. Will remain fluid at low temperatures (0°F).
4. Will not form insoluble gums or sludge excessively after 48 hours.
5. Will retain a broad spectrum of types of pesticides during a 24 hour sampling period.
6. Will have an acceptable collection efficiency for a broad spectrum of pesticides.
7. Is amenable to routine pesticide separation and cleanup procedures.

The use of cottonseed oil in this project has proved to be a fortunate first choice, but because it is a natural product, a semi-drying oil, and potentially subject to oxidative and polymerization reactions, a search for a non-natural coating should be fully investigated.

A cursory search for substitute liquid coatings to replace cottonseed oil was initiated using synthetic organic chemicals instead of refined natural oils.

The test procedure was relatively simple. The beads were coated with the test liquid and a pesticide collection module as described in Appendix B. The module was placed on the sampling shelter located outdoors. The flow was adjusted to 10 CFM, and the timer set for 48 hours. At the end of 1, 3, 24, and 48 hours the canister was observed, and a subjective decision made of the condition of the coating.

Several test coatings were investigated. The results are given in Table 31. Of the liquids screened, diethylene glycol monooleate, and Dow Corning Silicone Oil 550 fluid gave an acceptable coating. Ethylene glycol, propylene glycol and brake fluid were completely unacceptable primarily because they could not maintain a sufficient coating on the beads for the required 48 hour time period.

TABLE 31

Subjective Screening for Liquid Coatings

Liquid Coating	Air Flow CFM	Duration of Test, Hours 1	3	24	48
Ethylene Glycol	10	Beads Dry	Dry	Dry	Dry
Propylene Glycol	10	OK	OK	Partly Coated	Dry
Brake Fluid	10	Coating Not Acceptable			
Diethylene Glycol Monooleate	10	OK	OK	OK	OK
Dow Corning Silicone Oil 550 Fluid	10	OK	OK	OK	OK

SECTION XVI

SUMMARY

An eight station experimental airborne pesticides monitoring network was established using a prototype design pesticide collection system. Sampling was conducted for a 12 month period according to the random schedule of the National Air Surveillance Network at Winter Haven, Florida, Lubbock, Texas and in New York State at Buffalo, Naples, Rome, Jordan, Lafayette, and Syracuse.

Of the possible 208 samples, 202 were collected, giving a 97% collection rate. Four of the six samples missed were due to electrical power failures caused by blizzard conditions. Only two were lost due to equipment failure.

Analysis of the samples showed that pesticides were found in 69 samples (33.5%), and that they were collected, either singly or in combination on 17 sampling days out of 26 possible (65.4%). The chronological occurrence of the pesticides indicated seasonal appearance beginning in March and ending in October for the southern stations, and from April through September in the New York stations.

The overall concentration ranges, in nanograms per cubic meter for each pesticide, were aldrin, 0.22-2.15; DDE, 0.14-2.16; DDT, 0.54-1101; heptachlor, 0.09-1.32; malathion, 0.06-3.53; methyl parathion, 0.02-0.84; parathion, 0.03-1.42; and total 2,4-D acid, 1.15-1.54. No

DDD, endrin, or heptachlor epoxide were detected in any sample from any sampling site.

Pesticides were found at each station during the sampling year. The number of sampling dates pesticides found at each sampling site were 14 (53.8%) at Winter Haven, Florida; 10 (38.5%) at Buffalo; 6 (23.1%) at Rome; 8 (30.8%) at Jordan; 8 (30.8%) at Lafayette; 6 (23.1%) at Naples; 3 (11.5%) at Syracuse, and 13 (50%) at Lubbock, Texas.

Inspection of the pesticide concentration data and the suspended particulate matter data collected for each sample shows that there is no apparent correlation between the two. This observation, however, does not mean that there were no pesticides adsorbed on the surface of the suspended particulate matter collected, but that when the glass fiber filter mat and cottonseed oil coated glass beads are analyzed together, differentiation between adsorbed pesticides on the filter and those trapped in the cottonseed oil is not possible.

Pesticides other than the study pesticides may also be collected by the sampling system. Ethion, for instance, was found in nine consecutive samples from Winter Haven, Florida in concentrations ranging from trace to 66,700 nanograms per cubic meter.

Adjunct analytical studies indicated that the collection efficiency of the pesticides collection module is dependent on the absorption characteristics of each pesticide in cottonseed oil. The cold

storage stability test indicated that little change occurs in the quantities of pesticides stored under simulated collected sample conditions.

SECTION XVII

ACKNOWLEDGEMENTS

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SECTION XVIII

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SECTION XIX

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APPENDIX A

OPERATING PROCEDURES FOR THE PESTICIDE MONITOR

The following outline gives the instructions for the operation and maintenance of the complete pesticide collection assembly in the field:

1.0 Installation of Module (Canister)

1.1 Remove the canister from the shipping container and inspect the glass beads to insure that the beads are in the lower neck of the canister. If they are not, shake the canister so that the beads are compacted and fall into the neck.

Care should be taken to prevent the Teflon discs in the shipping container from becoming contaminated. The container lid should be replaced as soon as the canister is removed.

1.2 Place the canister on the stainless steel flange and tighten the bolt on the lower ring. Secure the canister with both toggle clamps. When fully tightened the red clamp handles should be in a vertical position.

2.0 Operation of Total Station

2.1 Connect the timer to the power cord. Switch the timer on and allow the blower to run for approximately one minute. Adjust the flow to 10 CFM. The flow is adjusted by means of the bleed valve located to the rear of the canister. The flow meter is located below the shelf and is calibrated in cubic feet per minute (CFM). The meter float read line is shown in Figure 1.

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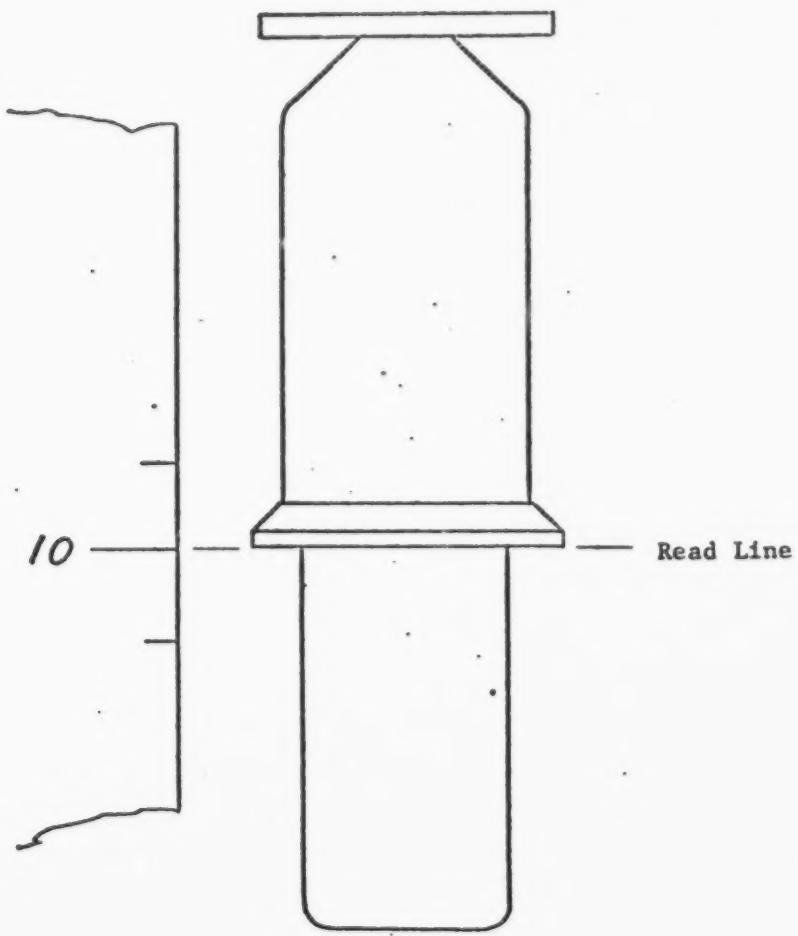
FIGURE 1

Flow Meter Float



2.1.1 Switch timer off. Turn the timer dial clockwise to the present time and day. Set the adjustable stops to correspond from midnight to midnight of the scheduled sampling day. The bright stop turns the blower on and should be positioned on the disc at the beginning of the sampling day. That is, the bright stop must reach the red pointer first when the disc is rotated clockwise. The black stop turns the blower off. The sampling days are listed on the schedule provided and can also be found labeled on the large upper coupling on the canister.

2.1.2 After the sampling run, before removing the canister, switch the blower on for approximately one minute and record the final flow on the data record sheet enclosed (Figure 2).

2.1.3 Fill out data record including any pertinent remarks.

2.1.4 Switch off blower and disconnect the power supply to the timer.

2.1.5 Remove the canister and place it and the data record sheet in the shipping container (until November 27, 1971)

Syracuse University Research Corporation
Life Sciences Division
Merrill Lane, University Heights
Syracuse, New York 13210

2.1.6 For any servicing, or malfunction, of the equipment please call collect to:

Bill Compton
1-315-477-8525

FIGURE 2

PESTICIDE MONITORING NETWORK

DATA RECORD

Location _____

Schedule Sampling Date _____

Actual Sampling Date _____

Initial Flow Reading _____

Final Flow Reading _____

Remarks:

A

Syracuse University Research Corporation, Merrill Lane, University Heights, Syracuse, New York 13210 tel 315 477 7077

APPENDIX B

PREPARATION OF AIRBORNE
PESTICIDES COLLECTION MODULES

The following is a stepwise outline of the procedure used to prepare the pesticide collection module for assembly, sampling and shipment to the field stations.

1.0 Preassembly Cleaning of Module Parts

1.1 Glass Reducers and Beads

The steps listed below are to be followed for adequate cleaning of all the glass modular parts before assembly.

1.1.1 Soak all parts in technical grade acetone.

1.1.2 Wash in chromic acid cleaning solution.

1.1.3 Rinse thoroughly with distilled water.

1.1.4 Rinse with pesticide grade acetone.

1.1.5 Dry the article with a jet of dry, filtered, compressed air.

1.2 Coupling and Metal Parts

1.2.1 Couplings

Due to exposure to wind-borne dust at the sampling sites, special precautions must be taken to assure that all of the parts composing the coupling are debris-free.

1.2.1.1 Disassemble the coupling completely.

1.2.1.2 Soak in distilled water overnight.

1.2.1.3 Remove from distilled water, and wipe each part with a lint-free laboratory towel.

1.2.1.4 Rinse the Teflon spacer with pesticide grade acetone.

1.2.2 Metal Parts

The metal parts referred to in this section are the 10 mesh

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stainless steel screen used in the sampling module to keep the glass beads contained in the bottom of the canister, and the steel spring used to keep the screens in place.

1.2.2.1 Wash each part thoroughly with technical grade acetone.

1.2.2.2 Wash in chromic acid cleaning solution.

1.2.2.3 Rinse with distilled water.

1.2.2.4 Rinse with pesticide grade acetone.

1.2.2.5 If it is necessary, before Step 1.2.2.1, place the metal parts in an ultrasonic cleaner with nonionic laboratory cleaner, and clean for 10 minutes.

2.0 Assembly of Module Parts

2.1 Preparation of glass fiber filter

The glass fiber filter to be used in the collection module is the Mine Safety Appliance Catalog #CT-75428 flash-fired glass fiber filter. The filters are cut to size (120 mm diameter) prior to the preparation described below:

2.1.1 Place filter in a petri desh (Kimble No. 8-757-2E Disposable Polystyrene 150 mm x 18 mm) whose top and bottom have been assigned an identification number.

2.1.2 Place the opened petri plate containing the filter in a desiccating chamber for 24 $\pm$ 2 hours.

2.1.3 Remove the plate, quickly cover, and transport to the analytical balance for taring. Handle the filter mat with forceps only.

2.1.4 Tare the filter and record the tare weight directly on the top petri dish. Record the weight on the master data card.

2.1.5 Store the petri dish containing the filter until ready for use.

2.2 Preparation of glass beads

The glass beads are to be prepared directly before use. The beads are to be prepared in the following manner:

2.2.1 Measure 140 ml. of clean glass beads in a graduated cylinder. The beads used were a polished, smooth surface glass.

2.2.2 Transfer the beads to a 500 ml. Erlenmeyer flask, prepared as in Section 1.1. Add 3 ml. of cottonseed oil.

2.2.3 Swirl the Erlenmeyer flask until the glass beads are uniformly coated.

2.3 Assembly of module parts.
The module is to be assembled using the following steps:

2.3.1 Reassemble the couplings.

2.3.2 Place the large (10 mesh) stainless steel screen in the reducer.

2.3.3 Insert the spring in the glass reducer so that it rests directly in the center of the screen.

2.3.4 Place the filter on the large 10 mesh stainless steel screen. Carefully insert the filter on the screen into the four inch coupling so that the filter faces outward.

2.3.5 Attach the coupling to the reducer in such a manner that the spring rests directly in the center of the screens.

2.3.6 Gently tighten the coupling to the reducer.

2.3.7 Invert the canister so that it rests on the four inch coupling.

2.3.8 Add the glass beads prepared in Section 2.2.3 above to the glass reducer.

2.3.9 Place the small (24 mesh) stainless steel screen in the 2 inch coupling.

2.3.10 Attach the 2 inch coupling to the bottom of the glass reducer and tighten.

3.0 Coding of the assembled sampling module.
The following laboratory coding system was used to identify each sample.

3.1 A coding letter was assigned to each module. The coding designations were:

Location	Identification Letter
Lubbock, Texas	T
Winter Haven, Florida	F
Buffalo, New York	B
Naples, New York	N
Rome, New York	R
Jordan, New York	J
Syracuse, New York	S
Lafayette, New York	L

3.2 A sampling date was assigned as well. This included the month, day, and year.

3.3 The laboratory code was then assigned for each station and date. Example: the assigned sample designation for Lubbock, Texas for December 21, 1970 was T122170.

3.4 On a master sheet, the filter number and tare weight of the filter was recorded for the properly coded module.

3.5 An identification sticker was attached to each module indicating the station to be sampled and the date of sampling. This avoided confusion for the field station personnel servicing more than one monitor.

APPENDIX C

SHIPMENT OF SAMPLING MODULES

Shipment of the prepared sampling modules was done in the following manner:

1.0 Shipment of Sampling Modules

1.1 Preparation for shipment
Each assembled sampling module was placed in its individual aluminum shipping container. After insertion into the shipping container, the following items were placed inside the container:

1.1.1 Data record sheet to record sampling data.

1.1.2 Return address labels. Pre-prepared REA prepaid shipping forms or sufficient postage.

1.1.3 On the outside of the container, proper address labels are to be attached to insure proper delivery.

1.2 Shipment
Shipment was made by the mode indicated and the destinations listed below:

1.2.1 Railway Express (REA), prepaid:

1.2.1.1 Lubbock, Texas:

Mr. Lee Orr
City-County Health Department
P. O. Box 2548
Lubbock, Texas 74908
806-762-6411, Extension 352

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APPENDIX C

SHIPMENT OF SAMPLING MODULES

Shipment of the prepared sampling modules was done in the following manner:

1.0 Shipment of Sampling Modules

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1.2.1.1 Lubbock, Texas:

Mr. Lee Orr
City-County Health Department
P. O. Box 2548
Lubbock, Texas 74908
806-762-6411, Extension 352

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1.2.1.2 Winter Haven, Florida

Mr. Gene McNeil
Department of Air and Water Pollution Control
West Central Region
P. O. Box 944
225 Avenue D, N.W.
Winter Haven, Florida 33880
Att: Mr. R. P. Barker
813-294-3287

1.2.1.3 Buffalo, New York

Mr. W. F. Millerschoen
Erie County Department of Health
134 Eagle Street
Buffalo, New York 14202
716-846-6370
Att: Dr. William J. Mitchell
716-846-8529

1.2.1.4 Naples, New York

Mr. Haynes
Water Control Chemist
Widmer's Wine Cellars
Naples, New York 14512
315-374-6311

1.2.2 Hand-delivered by SURC:

1.2.2.1 Onondaga County Air Pollution Monitoring Station, Downtown Syracuse. The trailer is located behind the Onondaga County Steam Station, just south of the City-County Public Safety Building and just north of the Everson Museum. Entry to the trailer may be made through the County Parking Lot at the

State Street entrance. Delivery was made to the following people:

(a) Mr. Edward Kawryga

(b) Mr. Graves

These gentlemen are employees of the Onondaga County Department of Health, Department of Air Pollution Control, 300 South Geddes Street, Syracuse, New York 13204, 315-477-1853. Either one or both people are located there until 4:30 p.m. each day. Two containers were dropped off, and two sample containers from the previous time picked up.

1.2.2.2 New York State Air Pollution Monitoring Station. This trailer is located directly southwest of the Administration Building on the grounds of the Metropolitan Syracuse Treatment Plant (Sewage) on Hiawatha Blvd. This trailer is white and has no windows. The general location is at the southeast end of Onondaga Lake. Delivery is to be made to the following person:

Mr. James Creedon

315-474-5951, Extension 255

Mr. Creedon should be located there until 4:30 p.m. each day. Only one container was dropped off and one sample container from the previous time picked up.

Mr. Creedon is an employee of the Division of Air Resources, New York State Department of Environmental Conservation. His immediate supervisor is:

Mr. David Prosser
Regional Engineer
Division of Air Resources
Central New York Regional Office
Department of Environmental Conservation
677 South Salina Street
Syracuse, New York 13202

The Syracuse, New York station was serviced by the Onondaga County Department of Health Personnel. The Rome, New York station was serviced by Mr. Creedon.

1.3 SURC Operated

The station located at Lafayette, New York was operated and serviced by SURC Air Pollution Laboratory personnel.

2.0 Sampling Schedule

The sampling schedule used to run the pesticide network was the National Air Surveillance Network Random Sampling Schedule for 1970 and 1971.

The shipping time estimates were formulated to insure that the containers would arrive well before the scheduled sampling date. The shipping schedule was designed from shipping data time estimates which are assumed to be average delivery times. The following table shows these time estimates:

Station	Carrier	Shipping Time, Days
Lubbock, Texas	REA Air Express	2
Winter Haven, Florida	REA Air Express	3
Buffalo, New York	REA Air Express	2
Naples, New York	Parcel Post	2
Rome, New York	Hand Carried	1

C

Station	Carrier	Shipping Time, Days
Jordan, New York	Hand Carried	1
Syracuse, New York	Hand Carried	1
Lafayette, New York	Hand Carried	1

APPENDIX D

ANALYTICAL REAGENTS AND SOLVENTS

1.0 Introduction

The reagents and solvents used during the course of the pesticide analytical sections of this project were selected or prepared in such a manner that substances which could cause degradation, adsorption, or interfere with the determinative step were absent. The general guidelines established by the Food and Drug Administration (1), and the Perrine Primate Laboratory (2), were followed.

Some reagents were specially prepared in the laboratory for use in derivative formation, for example, diazomethane for methylation procedures, or special extraction of solid reagents to remove possible interferents. Special precautions were taken to prevent potential contamination from the laboratory compressed air supply when air was required for drying or evaporative procedures.

1.1 Solvents

1.1.1 Acetone. Reagent Grade. Used to rinse glassware.

1.1.2 Acetone. Pesticide Quality. Used to final rinse glassware, and used in analytical steps requiring acetone.

1.1.3 Acetonitrile. Pesticide Quality. Used in all analytical steps requiring acetonitrile.

1.1.4 Alcohol. USP ethanol, reagent grade. Used for rinsing and cleaning purposes.

1.1.5 Alcohol. Pesticide Quality ethanol. Used in all analytical steps requiring ethanol.

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1.1.6 Chloroform. Pesticide Quality. Used in all analytical steps requiring chloroform, and for rinsing purposes.

1.1.7 Ethyl Ether. Pesticide Quality. Used in all analytical steps requiring ethyl ether and for rinsing purposes.

1.1.8 2% V/V Ethanol in Ethyl Ether. Used for Florisil column-elution.

1.1.9 Hexane. Pesticide Quality. Used in all analytical steps requiring hexane, and for rinsing purposes.

1.1.10 Methanol. Pesticide Quality. Kept available for rinsing purposes.

1.1.11 Petroleum Ether. Pesticide Quality. Used in all analytical steps requiring petroleum ether. Boiling Range, 30 - 60°C.

1.1.12 2,2,4-Trimethylpentane. Pesticide Quality. Used in all analytical steps requiring trimethlpentane.

1.2 Solid Reagents and Auxiliary Supplies

1.2.1 Cotton. Absorbent. Prerinsed before use with pesticide quality acetone and chloroform.

1.2.2 Diazald (N-methyl-N-nitroso-p-toluenesulfonamide) Aldrich Cat. No. 2800-0. For preparation of diazomethane.

1.2.3 Florisil, P.R. Grade, 60-100 mesh: Fisher Cat. No. F-100. For special preparation see Section 2.0 below.

1.2.4 Glass Wool. Pyrex. Prerinsed before use with pesticide grade acetone and hexane, or as in Section 3.0 below.

1.2.5 Sodium Bicarbonate. Reagent Grade.

1.2.6 Sodium Chloride. Reagent Grade. For special preparation, see Section 3.0 below.

1.2.7 Sodium Sulfate, anhydrous. Granular. For special preparation, see Section 3.0 below.

1.2.8 Sulfuric acid, Reagent Grade. Sp. Gr. 1.84.

1.2.9 Air, Laboratory Compressed. Passed through a Pall-Trinity Particulate filter and a 30 cm column of Type 4A Molecular Sieve, 1/16 inch pellets.

1.2.10 Water, Distilled. Taken directly from tin-lined distilled water storage tank. Water is passed through an ion exchange column before distillation.

2.0 Preparation of Florisil for Laboratory Use

2.1 Introduction

Florisil was purchased in 25 pound lots. Historically, Florisil has been known to contain quantities of contaminants which will interfere with electron capture detection of chlorinated pesticides. Since Florisil is packed in polyethylene bags in lots of this size, some plasticizer may be extracted by the Florisil, and subsequently may appear as a contaminant. As a result, steps must be taken which will minimize this and other contaminants which may be contained or absorbed by the Florisil. The following procedure has been used with success:

2.1.1 Place approximately 200 g of Florisil in a 60 x 180 mm cellulose single thickness extraction thimble and place the thimble in a Soxhlet extraction apparatus. Add a sufficient quantity of 50% ethyl ether-petroleum ether to allow efficient cycling. Adjust applied heat carefully.

2.1.2 Adjust the cycling rate of the extraction so that each cycle takes approximately 3 - 4 minutes. Extract the Florisil for at least six hours. Remove the thimble,

place the Florisil in an evaporating dish, and allow to air dry at room temperature for a few hours or place in a low temperature vacuum oven until the remaining solvent is removed.

2.1.3 The Florisil is then placed in an oven at 130°C for 24 hours. The conditioned Florisil is then used as quickly as possible. Enough Florisil is prepared at one time in this manner to provide for the projected work load for several days. If large quantities are required, the Florisil is stored at 130°C in the dark and used as required.

2.1.4 Because of variations in absorptive capacity of Florisil, each batch of Florisil should be standardized by absorption of lauric acid as described in Section 121.32 in the Pesticide Analytical Manual, Volume 1, regardless of source (1). Calculate the lauric acid value and the equivalent weight for the batch of Florisil. The proper elution of pesticides should be verified by Section 121.33, Pesticide Analytical Manual, Volume 1 (1).

2.1.5 Should the Florisil elution pattern not be satisfactory, the batch of Florisil may be washed with hot distilled water and recalcined at 1250°F for 2.5 hours according to the method of Hall (3). The treated Florisil should be restandardized by lauric acid absorption and the elution pattern of pesticides verified.

3.0 Preparation of Sodium Sulfate, Sodium Chloride and Glass Wool for Laboratory Use

3.1 Sodium sulfate, sodium chloride, and glass wool used in the procedure may contain interfering substances. As a result, these materials are carried through the same procedure used in Section 2.0 for Florisil.

4.0 Preparation of Diazomethane

4.1 Introduction

The procedure described here is identical to that described in the Pesticide Analytical Manual Volume I, Sections 221.12c.(1), with the exception that all ground glass joint equipment is used. Each male joint in the system has been equipped with a Teflon sleeve to prevent potential rapid decomposition of the synthesized diazomethane. Only smooth, unchipped, joints are used.

4.2 Apparatus for the Preparation of Diazomethane

4.2.1 Description of Apparatus

The apparatus used to prepare the diazomethane is shown in Figure 1. The component parts of the glassware are identified as follows:

Kontes Glass Company (or equivalent):

K-16750 Adapter, connecting, 24/40

K-18100 Adapter, gas inlet, 24/40

K-20600 Adapter, vacuum take-off, 24/40

K-45200 West condenser, jacket length 300mm, 24/40

K-60100 Flask, boiling, round bottom, single neck, 24/40; one 250 ml capacity, two 200 ml capacity

K-63628 Funnel, separatory with 24/40 joint and Teflon stopcock, 500 ml capacity

K-66825 Drying tube

K-67600 Teflon sleeves, 24/40

Miscellaneous Items:

Magnetic stirring hotplate

Teflon coated magnetic stirring bars, 1/2 inch and 3 inch

Beakers, two 1000 ml capacity, one 2000 ml capacity

Laboratory jacks, two small size.

One large thermometer, -20 to +150°C.

D

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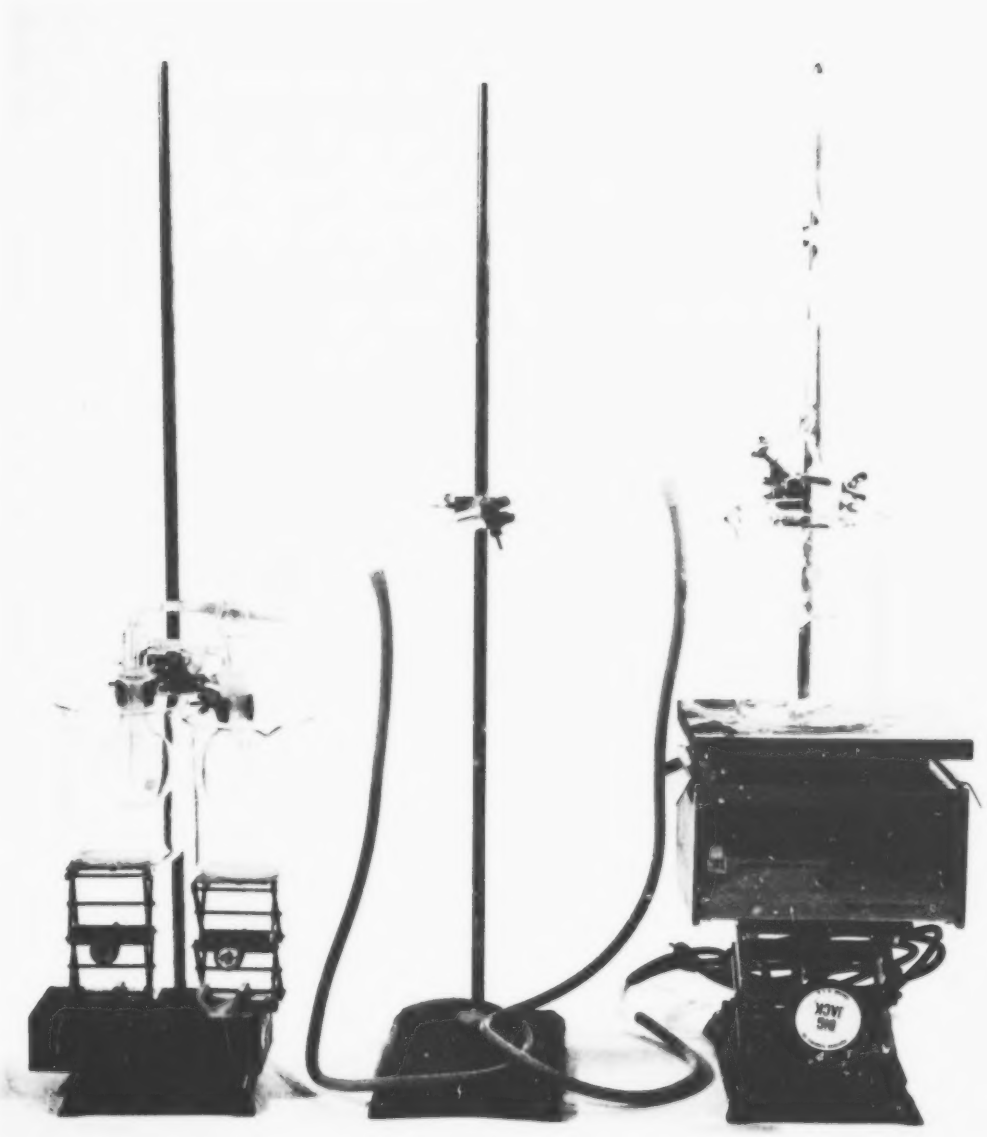

Figure 1 Diazomethane Preparation Apparatus

In a well ventilated hood, assemble the separatory funnel, connecting adapter, a 250 ml round bottom flask, and the condenser. Connect the condenser to a 200 ml round bottom flask with vacuum take-off adaptor. Connect the take-off arm of the adapter to the inlet of the inlet adapter with a short piece of Tygon tubing. The inlet adapter is then placed in another 200 ml round bottom flask containing 20 ml of ethyl ether. The inlet tube must extend below the level of the ethyl ether.

As a water bath for the distilling set up, place a two liter beaker on a magnetic stirring hotplate, maintaining the temperature at 70°C.

4.3 Preparation

Dissolve 6g of potassium hydroxide in 10 ml of distilled water in the distilling flask (no heat). Add 35 ml Carbitol (diethylene glycol monoethyl ether), a Teflon stirring bar, and another 10 mls of ether. Connect the distilling flask to the condenser and immerse the distilling flask in the water bath. By means of the dropping funnel, add a solution of 21.5g Diazald in 140 ml of ethyl ether over a period of 20 minutes. After distillation is apparently complete, add another 20 ml of ethyl ether and continue distillation until the distillate is colorless. Combine the contents of the two receiving flasks in a glass bottle (without a ground glass neck), stopper with a cork, and freeze overnight. Decant the diazomethane from the ice crystals into a glass bottle, stopper with a cork, and store in a freezer until ready for use. The final solution may be stored up to six months without marked deterioration.

5.0 Routine Handling of Laboratory Glassware

5.1 The glassware used throughout all phases of analysis must be scrupulously cleaned. The following procedures should be followed for routine cleaning of glassware.

5.1.1 Tap water rinse all glassware immediately after use.

5.1.2 Rinse with technical grade acetone.

5.1.3 Soak for 15 minutes in 6N sodium hydroxide solution.

5.1.4 Tap water rinse the glassware from 5.1.3.

5.1.5 Soak in chromic acid cleaning solution.

5.1.6 Tap water rinse the chromic acid washed glassware.

5.1.7 Distilled water rinse the glassware from 5.1.6 above.

5.1.8 Rinse with pesticide quality acetone.

5.1.9 Rinse with pesticide quality solvent that will be used immediately before use.

APPENDIX E

EXTRACTION AND CLEANUP OF

COLLECTED FIELD SAMPLES

1.0 Introduction

The separation of airborne pesticides from the collecting media of the field sampling assembly is conducted in two stages. First, the collection module parts are extracted with hexane. Then the hexane extract is subjected to a cleanup procedure which separates the pesticides for final analysis.

The collection module was designed so that suspended particulate matter is collected at the same time as pesticide sampling occurs. The air volume flow rate is sufficient that a weighable quantity of material is collected on the filter. The quantity of particulate matter collected provides important adjunct information in relation to potential pesticides collected at the time of sampling. Therefore, prior to the extraction stage, the tared glass fiber filter mat is reweighed.

2.0 Glass Fiber Filter Mat Weighing Procedure

2.1 Remove the 4 inch coupling containing the filter carefully from the reducer. Place the screens in a 9" x 12" x 2" Pyrex dish.

2.2 Transfer the filter carefully with forceps to the petri plate marked with the laboratory sample code for that sampling date and the tare weight.

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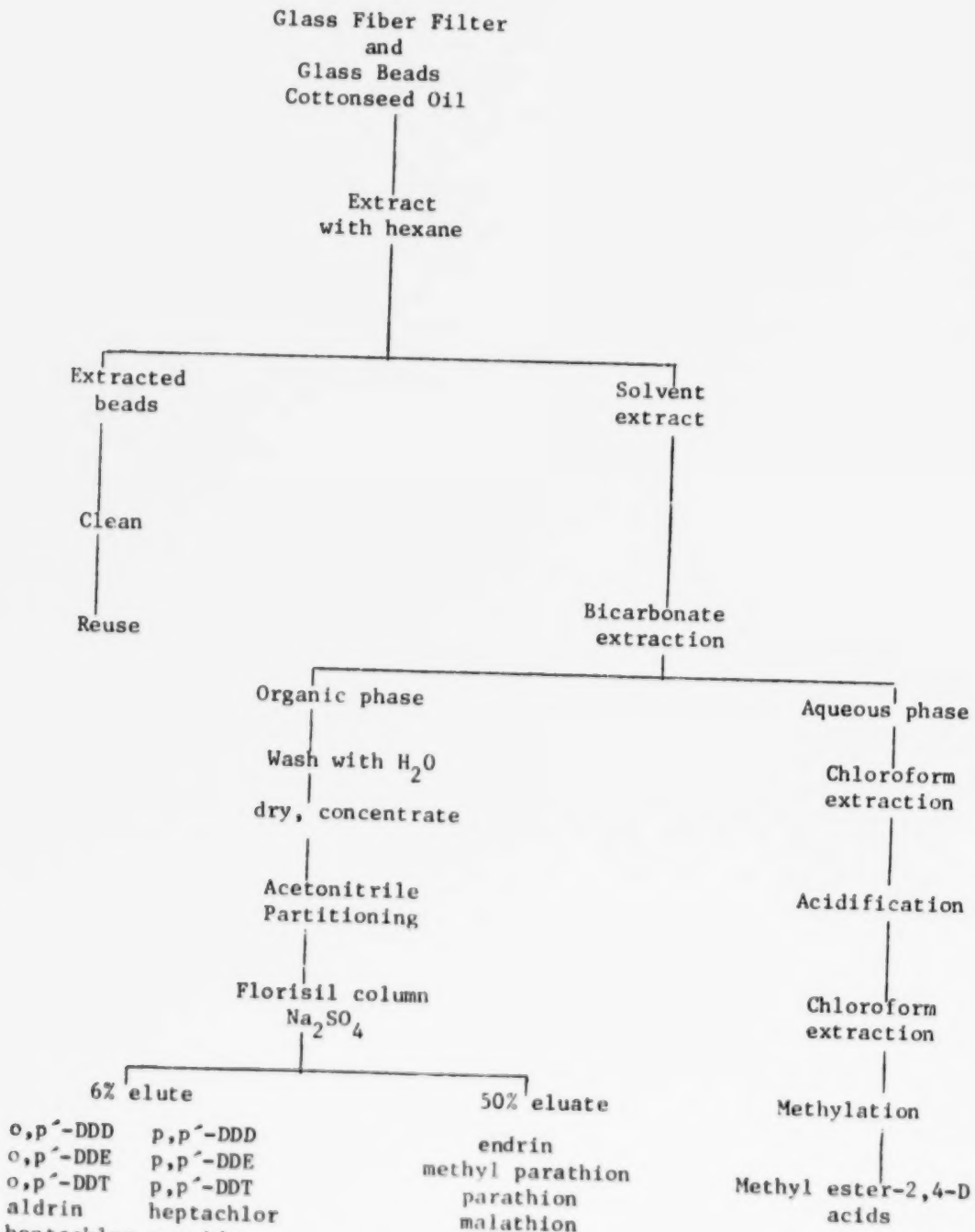
FIGURE 1

Glass Beads Coated with Cottonseed Oil and Glass Fiber Filter
Separation and Cleanup Procedures



2.3 Place the open dish, top plate on the bottom, in the drying chamber for 24 ± 2 hours.

2.4 Remove the plate, quickly cover, and transport to the analytical balance for weighing.

2.5 Weigh to the closest 0.1 mg. Record the weight on the master data card.

3.0 Extraction of Collecting Media

3.1 Remove the small coupling and screen. Carefully transfer the coated glass beads to a 123 x 43 mm paper filter thimble.

3.1.1 The thimbles are to be pre-extracted for two hours at a cycle rate of six per hour in a Soxhlet extraction apparatus with pesticide grade hexane, and stored in a desiccator before use.

3.2 Loosely fold the reweighed glass fiber filter from 2.5 above, and place in the thimble over the beads.

3.3 Place the glass reducer, screens, and spring in the Pyrex dish (Section 2.1). Carefully rinse each part with hexane. Rinse the Teflon-coated flanges of the shipping container into the dish and, transfer the combined rinses to the Soxhlet extraction apparatus containing the thimble filled with the glass beads and filter. Rinse the dish three times with hexane, transferring the rinses directly to the extraction apparatus.

3.3.1 Keep the total volume of hexane at approximately 250 ml.

3.4 Extract the beads and the filter for two hours starting with the first cycle. The cycling rate should be at least once every 10 minutes.

3.5 For some selected samples it will be necessary to separate the glass fiber filter and coated glass beads for separate analysis. In this case only the filter is extracted in the Soxhlet extraction apparatus. The glass beads are then extracted in another apparatus.

3.6 After the extraction period is over, the extract is ready for the cleanup procedure.

4.0 Cleanup and Separation Procedures for Collection Media Extracts

4.1 Introduction

The analytical scheme to be followed for the analysis of the study pesticides is given in Figure 1. The study pesticides in this case are the following: (1) Methylation-methyl esters of 2,4-D, (2) 6% Ethyl Ether in Petroleum Ether Eluate-aldrin, o,p´-DDD, p,p´-DDD, o,p´-DDE, p,p´-DDE, o,p´-DDT, and p,p´-DDT, heptachlor and heptachlor epoxide, (3) 50% Ethyl Ether in Petroleum Ether Eluate-endrin, methyl parathion, malathion, and parathion.

4.2 Separation of Chlorinated and Organophosphorus Pesticides from 2,4-D Acids

Quantitatively transfer the 250 ml hexane extract to a 500 ml separatory funnel equipped with a Teflon stopcock. Add 35 ml of ethanol and 50 ml of 4% sodium bicarbonate solution to the separatory funnel. After venting, shake vigorously for one minute. When the layers separate, drain the lower aqueous layer into another 500 ml separatory funnel. Repeat the extraction twice using 15 ml of ethanol and 40 ml 4% sodium bicarbonate each time. Wash the hexane layer twice with 100 ml of distilled water. Pass the hexane solution containing possible

chlorinated and organophosphorus pesticides through 30 g. of anhydrous sodium sulfate into a beaker and proceed with the hexane solution directly to the acetonitrile partition step.

4.3 Methylation Procedure

Combine the aqueous phases from 4.2 and extract twice with 25 ml chloroform, shaking for 30 seconds each time. Discard the chloroform washes and carefully acidify the aqueous solution with 25 ml 10% aqueous sulfuric acid (make certain that the solution is acidic). Extract the acidified solution three times with 30 ml of chloroform each time, shaking 30 seconds each time. Drain each chloroform extract through a plug of cotton in a small glass funnel into a 250 ml Phillips beaker. Rinse the cotton plug with chloroform after the third chloroform extract has filtered through. Carefully remove the glass wool and replace the funnel in the 250 ml Phillips beaker. Add boiling chips and evaporate the sample until the solvent is removed on the steam bath. Remove the final traces of chloroform with the aid of ethyl ether and a jet of clean, dry air.

Place the beaker containing the chlorophenoxy residues in the hood away from the steam bath. Rinse the sides of the beaker with a small quantity of ethyl ether, and add 2 ml of diazomethane. Let the mixture stand for 10 minutes with occasional gentle shaking, then evaporate the solvent with a gentle stream of air. Transfer the sample to a glass stoppered test tube (12 ml) with petroleum ether. Evaporate the solution to dryness with a gentle stream of air. Dissolve the residue in 2,2,4 - trimethylpentane for chromatography.

4.4 Acetonitrile Partition Step

Evaporate the hexane, from the bicarbonate wash, to approximately 5 ml on a steam bath with the aid of a stream of air. Quantitatively transfer the extract from the beaker to a 125 ml separatory funnel with a total of 10 ml petroleum ether. Add 30 ml of acetonitrile, previously saturated with hexane, to the separatory funnel and shake vigorously for 1 minute. Drain the bottom acetonitrile layer into a 1 liter separatory funnel containing 100 ml hexane and 700 ml 2% sodium chloride solution. Extract the cottonseed oil hexane mixture with three more 30 ml portions of acetonitrile saturated with hexane, shaking for 1 minute each time. Combine the acetonitrile extracts in the 1 liter funnel and shake for 30 seconds. Drain the aqueous layer into a second 1 liter separatory funnel and extract again with 100 ml hexane, shaking for 30 seconds. Discard the aqueous layer and wash the combined hexane layers with two 100 ml portions of distilled water. Pass the washed hexane through 30 g of anhydrous sodium sulfate into a beaker. Wash the separatory funnel and sodium sulfate with two 20 ml hexane. Evaporate the hexane to approximately 20 ml on a steam bath with the aid of a stream of air. Proceed to the Florisil column step.

4.5 Florisil Column Cleanup

Prepare a 22 mm inside diameter chromatographic column by filling with the equivalent weight of Florisil determined in 2.1.4 and 0.5 inches of anhydrous sodium sulfate. Wash the column with 50 ml petroleum ether. As the solvent level reaches the top of the column, but before the surface is exposed, add the concentrated extract from the acetronitrile step and collect the eluate. Rinse the beaker with two

10 ml portions petroleum ether; and as the solvent level reaches the top of the column, add 200 ml of 6% ethyl ether (containing 2% by volume ethanol) in petroleum ether. Adjust the eluate flow rate to approximately 5 ml/min. Change receivers as the solvent reaches the top of the column and elute with 200 ml of 50% ethyl ether (containing 2% ethanol by volume) in petroleum ether. Concentrate each fraction to 10 ml for gas liquid chromatographic analysis on a steam bath under a gentle air stream.

APPENDIX F

GAS CHROMATOGRAPHIC ANALYSES OF EXTRACTS FROM
THE SEPARATION AND CLEANUP PROCEDURES

1.0 Introduction

The result of the separation and cleanup procedures outlined in Appendix 5 were three fractions ready for gas chromatographic analysis. The 6% ethyl ether-petroleum ether eluate was analyzed for the following study pesticides: aldrin; o,p´-DDD, p,p´-DDD; o,p´-DDE; p,p´-DDE; o,p´-DDT; p,p´-DDT; heptachlor, and heptachlor epoxide. The 50% ethyl ether-petroleum ether fraction was analyzed for endrin, methyl parathion, malathion, and parathion. The methyl ester fraction was analyzed for the derivative methyl esters of 2,4-D and the results expressed as total 2,4-D acids.

2.0 Instrumentation

2.1 Gas Chromatographs - General

The pesticide analyses were performed on three Micro Tek Model MT-220 gas chromatographs. Each unit was equipped with a Nickel-63, paralled plate, electron capture detector operated in the DC mode. Two of the units were equipped with high temperature flame photometric detectors which were operated in the phosphorus mode.

2.2 Gas Chromatographic Columns

2.2.1 Column Packings. Four gas chromatographic column packings were used during the course of the study. These were (a) 1.5% OV-17/1.95% QF-1 on 80-100 mesh Supelcoport, (b) 4% SE-30/6%

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QF-1 on 80-100 mesh Supelcoport, (c) 5% OV-210 on 100-120 mesh Gas Chrom Q, and (d) 10% DC-200/1.5% QF-1 on 80-100 mesh Gas Chrom Q. Packing (a), (b), and (c) were supplied by the Perrine Primate Laboratory, while packing (d) was prepared using the mixed packing technique described in Section 302.12b and Section 203.12a (1), in the Pesticide Analytical Manual, I (').

2.2.2 Column Packing Conditioning

Only 6' x 4 mm glass U-shaped columns were used during the course of the study. Prior to filling, the empty column was washed with chromic acid cleaning solution, rinsed thoroughly with distilled water, then rinsed again with pesticide quality acetone. The columns were packed by recognized packing techniques (2) and the ends plugged with silanized glass wool. The column was placed in the gas chromatograph oven and conditioned at 245°C for 3-5 days with a nitrogen carrier gas flow of 25-50 ml/min. The column was not connected to the detector during conditioning. The inlets to the detectors were plugged during the conditioning phase. A nitrogen purge flow of approximately 50 ml/min was maintained through the electron capture detectors during this time.

After the conditioning period was over, the columns were treated with Silyl 8, and then with a conditioning mixture of test pesticides according to the technique of Perrine (2). The columns were then connected to the detectors, and the column-detector system allowed to equilibrate overnight.

2.2.3 Selection of Optimum Gas Chromatographic Conditions

Each column-detector system was handled in the same manner. In order to obtain the optimum response, separation and sensitivity the following stepwise procedure was used.

2.2.3.1 Prepare a carrier gas rotometer flow curve for each particular column-detector combination. Very rarely are the flow curves identical from one column-detector combination to another, so the calibration curve must be prepared for each detector-column combination. The rotometer calibration curve should be taken with all of the oven, detector, and other necessary heaters set at the recommended use temperatures. For electron capture systems, make certain that the purge flow is off.

2.2.3.2 Adjust the carrier gas flow to within 0.1 units of the recommended flow.

2.2.3.3 If the column-detector system has an electron capture detector, it is necessary to conduct a background current curve each time a new column is installed, or after the column has been in use for awhile. The method of Perrine (2) has been used in our laboratory, and has proven to be a good general method.

2.2.3.4 For other detector systems such as flame photometric detectors, it has been found that by optimizing the conditions of column use with an electron capture detector first, then that column may be transferred for use to another detector system, providing that all of the proper flow and temperature conditions are met.

2.2.3.5 Using a gas chromatograph equipped with an electron capture detector, after the carrier gas flow has been accurately set, an aldrin standard is injected in a concentration which will give approximately 50% full-scale strip chart recorder deflection at an input and output attenuation giving maximum sensitivity for the instrument. Starting with an oven pyrometer temperature of 170°C, inject the same volume of standard until the desired retention time for the column is obtained. Increase the oven temperature by 5°C increments and allow the temperature conditions to equilibrate before injecting again.

2.2.3.6 When the desired retention time for aldrin has been reached, adjust the purge flow until maximum peak height of the standard has been obtained, In no case, however, should the combination of column carrier gas flow and purge flow exceed the purge gas flow that was used to obtain the ideal background current profile of the detector.

2.2.3.7 At this point the system is ready for column evaluation. Using the operating conditions found above, inject 5 µl of mixed standards which will give approximately 50% response and examine the resulting chromatogram. By calculating the relative retention ratio of each pesticide with respect to aldrin, it is possible to calibrate the oven pyrometer by comparing the relative retention ratio of the pesticides with those published by Perrine (2). By noting the best temperature as indicated by the oven pyrometer, the optimum operating temperature may be maintained. Column efficiency may then be calculated to check the performance of the column in separating the pesticides. If the column effiency indicates that the column is satisfactory (approximately 3,000 theoretical plates based on p,p´-DDT), the column is checked for compound breakdown characteristics, using p,p´-DDT and endrin as the indicators. The breakdown products for, p,p´-DDT and endrin should ideally be less than 3% and 6%, respectively.

2.3 Linearity of Response and Limits of Detection

2.3.1 Introduction

The linearity of response of the detector must be determined in order to minimize errors in the quantitation of unknowns. The preparation of standard pesticide mixtures was patterned directly after that suggested by Perrine (2) for this study. The standard mixtures were composed of those pesticides expected to be found in each eluate from the separation and cleanup procedure. Therefore, a stock standard was prepared containing aldrin, o,p´-DDD, p,p´-DDD, o,p´-DDE, p,p´-DDE,

o,p´-DDT, p,p´-DDT, heptachlor, and heptachlor epoxide which represented the study pesticides in the 6% eluate. A stock standard containing aldrin, endrin, malathion, methyl parathion, and parathion was prepared for the 50% eluate. A stock solution of 2,4-D acid was prepared for the methyl ester of 2,4-D total acid determinations.

2.3.2 Linearity of Response

A series of working standards were prepared from the stock solutions given above. Since the concentration of potential pesticides collected was anticipated to be relatively low, the series of standards were prepared to cover this possibility. A typical series of 6% and 50% eluate pesticides concentrations are given in Table 1.

The standard mixtures are used for linearity checks for establishing the lower limit of detection of each pesticide, and for unknown identification purposes.

Injection of 5 ul of each of the standards, with subsequent plotting of concentration versus response, allows determination of the linearity of response for a specific detector.

2.3.3 Minimum Detectable Limits

A series of injections were made which allowed the calculations of minimum detectable concentrations for each of the study pesticides. The minimum detectable quantity is defined as that quantity of pesticide that yields a 10% of full scale strip chart recorder deflection with a 1% noise level.

Table 2 lists the minimum detectable quantity of each pesticide by electron capture detection using two different column packings, 1.5% OV-17/1.95% QF-1 on 80-100 mesh Supelcoport and 5% OV-210 on 100-120 mesh Gas Chrom Q. The relative retention ratios of each pesticide with respect to aldrin is also listed.

TABLE 1

Standard Pesticide Mixture for 6% and 50% Eluates - Typical Concentrations

Series C - 6% Eluate

Pesticide	C_1 pg/µl	C_1 pg/5 l	C_2 pg/µl	C_2 pg/5µl	C_3 pg/µl	C_3 pg/5µl	C_4 pg/µl	C_4 pg/5µl
Heptachlor	4.8	24.0	9.6	48.0	14.4	72.0	19.2	96.0
Aldrin	5.15	25.75	10.3	51.5	15.45	77.25	20.2	101.0
Heptachlor Epoxide	9.68	48.4	19.36	96.8	29.04	145.2	38.72	193.6
o,p´-DDE	10.40	52.0	20.80	104.0	31.20	156.0	41.6	208.0
p,p´-DDE	10.12	50.6	20.24	101.2	30.36	151.8	40.45	202.4
o,p´-DDD	9.90	49.5	19.80	99.0	39.60	198.0	59.4	297.0
p,p´-DDD	10.36	51.8	20.72	103.6	41.44	207.2	62.16	310.8
o,p´-DDT	10.80	54.0	21.60	108.0	43.20	216.0	64.8	324.0
p,p´-DDT	18.00	90.0	36.00	180.0	54.00	270.0	72.0	360.0

Series B - 50% Eluate

Pesticide	B_1 pg/µl	B_1 pg/5µl	B_2 pg/µl	B_2 pg/5µl	B_3 pg/µl	B_3 pg/5µl	B_4 pg/µl	B_4 pg/5µl
Aldrin	5.5	25.75	10.3	51.5	15.45	77.25	30.90	103.0
Endrin	19.32	96.60	38.64	193.2	67.62	338.0	96.66	483.3
Methyl Parathion	21.12	105.60	42.24	211.2	73.92	369.6	105.6	528
Parathion	21.20	106.00	42.40	212.0	74.20	371.0	106.0	530
Malathion	41.20	206.0	82.40	412.0	144.2	721.0	206	103.0

TABLE 2

Minimum Detectable Quantity of Test Pesticides by
Electron Capture Detection
(Nickel-63 Parallel Plate Detector)

Pesticide	1.5% OV-17/1.95% QF-1		5% OV-210	
	Minimum Detectable Quantity, pg	RRR*	Minimum Detectable Quantity, pg	RRR*
Aldrin	7	1.00	6	1.00
o,p'-DDD	24	2.70	37	2.52
p,p'-DDD	20	3.56	30	3.70
o,p'-DDE	30	1.83	19	1.91
p,p'-DDE	27	2.26	16	2.07
o,p'-DDT	21	3.18	27	2.67
p,p'-DDT	54	4.24	43	4.02
Endrin	58	2.96	28	3.33
Heptachlor	6	0.85	6	0.89
Heptachlor epoxide	15	1.56	18	1.58
Malathion	247	1.67	61	3.13
Methyl Parathion	42	1.47	90	2.74
Parathion	89	1.67	92	3.57
2,4-D Methyl Ester	60	0.46	150	0.69

*RRR = Relative Retention Ratio with respect to aldrin.

Table 3 lists the minimum detectable quantity of the organophosphorus pesticides under study, malathion, methyl parathion, and parathion, for three column packings: 4% SE-30/6% QF-1 on 80-100 mesh Supelcoport, 1.5% OV-17/1.95% QF-1 on 80-100 mesh Supelcoport, and 10% DC-200/1.5% QF-1 on 80-100 mesh on Gas Chrom Q.

Table 4 shows the gas chromatographic conditions used for each column to give optimum operating conditions.

3.0 Gas Chromatography of Sample Extracts

3.1 Introduction

When the optimum operating parameters for a particular column-detector system have been obtained, routine injection of the sample extracts may be performed. Selection of the column to be used was predicated on separation of the study pesticides in the 6%, 50%, and methyl ester 2,4-D extracts.

3.1.1 6% Eluates. Initial screening of the 6% eluates was done on a 1.5% OV-17/1.95% QF-1 column using an electron capture detector. This column separates all of the compounds expected to be found in the 6% fraction with no overlapping peaks. For confirmatory purposes either the 5% OV-210 column, or the 4% SE-30/6% QF-1 column with electron capture detection may be used.

An injection volume of 5 µl of the 10 ml eluate concentrate is used.

3.1.2 50% Eluate. Initial screening was done by injecting 5 µl of the 10 ml 50% eluate concentrate onto a 1.5% OV-17/1.95% QF-1 column with electron capture detection. This column separates malathion, methyl parathion, parathion, and endrin with no

TABLE 3

Minimum Quantity of Test Pesticides by Flame Photometric Detection (Phosphorus Mode) by Gas Chromatographic Column

Pesticide	4% SE-30/6% QF-1		1.5% OV-17/1.95% QF-1		10% DC-200/1.5% QF-1	
	Minimum Detectable Quantity, pg	RRR	Minimum Detectable Quantity, pg	RRR	Minimum Detectable Quantity, pg	RRR
Malathion	520	1.06	187	1.13	458	1.16
Methyl Parathion	140	1.00	78	1.00	184	1.00
Parathion	100	1.31	106	1.29	212	1.34

*RRR = Relative Retention Ratios with respect to methyl parathion.

TABLE 3

Minimum Quantity of Test Pesticides by Flame Photometric Detection (Phosphorus Mode) by Gas Chromatographic Column

Pesticide	4% SE-30/6% QF-1		1.5% OV-17/1.95% QF-1		10% DC-200/1.5% QF-1	
	Minimum Detectable Quantity, pg	RRR	Minimum Detectable Quantity, pg	RRR	Minimum Detectable Quantity, pg	RRR
Malathion	520	1.06	187	1.13	458	1.16
Methyl Parathion	140	1.00	78	1.00	184	1.00
Parathion	100	1.31	106	1.29	212	1.34

*RRR = Relative Retention Ratios with respect to methyl parathion.

TABLE 4

Gas Chromatographic Operating Conditions

Column		1.5% OV-17/1.95% QF-1 on 80-100 mesh Supelcoport	5% OV-210 on 100-120 mesh Gas Chrom Q	4% SE-30/6% QF-1 on 80-100 mesh Supelcoport	10% DC-200/1.5% QF-1 on 80-100 mesh Gas Chrom Q
Column Temperature		200°C	180°C	200°C	200°C
Inlet Temperature		225°C	225°C	225°C	225°C
Detector Temperature,	E.C.*	275°C	275°C	275°C	275°C
	F.P.D.**	200°C	200°C	200°C	200°C
Bucking Range, Amperes	E.C.	-2×10^{-8}	-2×10^{-8}	-2×10^{-8}	-2×10^{-8}
	F.P.D.	$+2 \times 10^{-8}$	--	$+2 \times 10^{-8}$	$+2 \times 10^{-8}$
Input Attenuation		10^2	10^2	10^2	10^2
Output Attenuation		2 - 128	2 - 128	32 - 128	16
Polarizing Voltage		D.C. Mode	D.C. Mode	D.C. Mode	D.C. Mode
Carrier Gas		Prepurified Nitrogen	Prepurified Nitrogen	Prepurified Nitrogen	Prepurified Nitrogen
Inlet Pressure, psig		50	50	50	50
Flow Rate, Carrier Gas		60 ml/min	46 ml/min	60 ml/min	120 ml/min
Purge Flow Rate, E.C.		20 ml/min	34 ml/min	20 ml/min	--
F.P.D. Conditions:					
Hydrogen Flow		150 ml/min	150 ml/min	150 ml/min	150 ml/min
Oxygen Flow		20 ml/min	20 ml/min	20 ml/min	30 ml/min
Air Flow		20 ml/min	20 ml/min	20 ml/min	20 ml/min
Chart Speed		1/2 inch/min	1/2 inch/min	1/2 inch/min	1/2 inch/min

*Electron Capture Detector

**Flame Photometric Detector

overlapping peaks. Confirmation of the organophosphorus pesticides was done by injecting 5 µl of the 50% eluate which had been reduced to a 1 ml volume, onto either a 10% DC-200/1.5% QF-1 or 1.5% OV-17/1.95% QF-1 column with a flame photometric detector operated in the phosphorus mode.

3.1.3 Methyl Esters of 2,4-D Acids. The methyl esters of the 2,4-D acids were screened using the 5% OV-210 column. The retention time of 2,4-D methyl ester is approximately 0.69 with respect to aldrin. The detection system used was electron capture.

3.2 Technique of Injection

Although there are several techniques used for sample or standard injection, the technique used during this project has been the solvent-flush method: using a 10 µl syringe, the volume of liquid held in the needle was carefully measured. This volume was noted for that syringe.

When preparing to inject, the liquid is drawn into the needle of the syringe, plus a small volume into the barrel. A small quantity of air, approximately 0.5 µl to 1 µl, or less if desired, is drawn into the needle. The solvent and air space are drawn into the syringe. The standard or sample is drawn into the syringe, so that the meniscus of the sample at the air bubble interface is near the 5 to 6 µl mark. The volume of sample is then adjusted so that the standard or sample in the needle and barrel of the syringe equals 5 µl.

This injection technique has been used throughout this project. The injection volume of standard or sample has been maintained at 5 µl as a uniform practice. It should be noted

that a source of contamination may be organic gases drawn into the syringe in the air bubble. Care should be taken to insure that no halogenated solvents are used outside of hooded areas in the vicinity of the gas chromatographs.

Once the proper quantities of liquids are drawn into the syringe, they are injected into the gas chromatograph. The needle is forced through the septum and inserted until the barrel of the syringe rests against the injection port. Simultaneously with penetration of the septum, the liquid is injected into the port, the syringe left in the port for approximately 5 seconds

3.3 Calibration Checks

Due to the nature of the sample extracts frequent calibration checks should be made to insure that the sensitivity of each detection system is maintained, and that column performance remains at a high level of efficiency. Therefore, 5 µl of the standard, which will give a response roughly equivalent to the unknown, is injected after each sample, or not less frequently than every two sample injections. Standards are injected at concentrations that give a response in the input and output attenuation used for the sample.

3.4 Identification and Quantitation of Pesticides

3.4.1 Identification

Suspected pesticides are identified using several techniques. The first is the determination of the retention time of the unknown peaks and comparing them with the retention time of

the standards run as calibration checks. This technique is especially useful because the nature of the samples require frequent checks.

Since the chromatograms of the air sample eluates are quite complex, two ancillary techniques were used. One involves the use of an internal standard; the other uses a peak enhancement technique for suspected pesticides. These techniques are necessary because of the relatively non-specific nature of electron-capture detection.

Using the internal standard technique, a pesticide of known retention time, but foreign to those to be determined is drawn into the syringe after the sample, two are separated by an air space. The suspected pesticides are then determined by comparing their relative retention ratios with the internal standard. This technique was used for all 2,4-D methyl ester samples.

The peak enhancement technique may be used in conjunction with the internal standard method. A quantity of a standard, or mixture of standards is injected along with the sample. If the peak shown by the sample coincides with that of the standard, then identification may be on that basis.

3.4.2 Quantitation

Quantitation of the identified pesticides was done by two techniques. Of the study pesticides, heptachlor, heptachlor epoxide and aldrin were quantitated by peak height. The peaks exhibited by these pesticides are very sharp and lend themselves to this type of quantitation.

The remaining study pesticides are quantitated by the standard peak height times width at half height, since the pesticides under study give symmetrical, relatively wide peaks.

APPENDIX G

FORTRAN IV COMPUTER PROGRAM

```
 11:34 JUN 28,'72 ID=04C2=F01
 JØB LSD,PEISEL
 ASSIGN F:107,(DEVICE,NØ)
 ASSIGN F:1,(DEVICE,9T),(INSN,ANY),(IN)
FØRTRAN LS,GØ
 EXT. FØRTRAN IV, VERSIØN DOO
```

```
C          AIR POLLUTION STUDY
C          L1073-05  -  PEISEL
C
      IMPLICIT INTEGER(A-Z)
      DIMENSION FILE(41)
      REAL Q(11)
      DOUBLE PRECISION P(11)
      REAL DGPST(14,26,8),KDC(8)
      REAL PGRMS(8,11)
      REAL TIME,FSTRT,FSTOP,TARE,GRSS,PRESS,NGRMS,PARTS,CF,AFAC,BFAC
      DOUBLE PRECISION STA,POL
      DIMENSION STALOC(7,8) ,POLUTS(7,11),DATE(2),CCLS(2,11)
      DATA STALOC/'33662001SYRACUSE, N. Y.      ',
     *            '33066001BUFFALO,N. Y.        ',
     *            '45334001LUBBOCK, TEXAS       ',
     *            '10488001WINTER HAVEN, FLA.   ',
     *            '33510001JORDAN, N. Y.        ',
     *            '33510002LAFAYETTE, N. Y.     ',
     *            '33512001NAPLES, N. Y.        ',
     *            '33506001ROME, N. Y.          '/
      DATA POLUTS/'51101   ALDRIN               ',
     *            '51106   ODD                  ',
     *            '51107   DDT                  ',
     *            '51109   HEPTACHLOR           ',
     *            '51118   DDE                  ',
     *            '51204   ENDRIN               ',
     *            '51208   HEPTACHLOR EPOXIDE   ',
     *            '51311   MALATHION            ',
     *            '51419   METHYL PARATHION     ',
     *            '51421   PARATHION            ',
     *            '54132   TOTAL 2,4-D          '/
      DATA CCLS/20,31,32,43,44,55,56,67,68,79,
     *          20,31,32,43,44,55,56,67,68,79,
     *          20,31/
C
      AFAC=.02832
      BFAC=1E6/AFAC
      DO 27 I=1,8
   27 KDC(I)=0
   20 CALL HUFFERIN(1,0,FILE,41,N)
   36 GO TO (36,37,30,37),N
   37 DECODE(164,10,FILE),CODE,STA,DATE,TIME,FSTRT,FSTOP,PRESS,TARE,GRSS
     *                   ,(P(I),Q(I),I=1,11)
   10 FORMAT(A1,A8,A4,A2,I4,2F3.1,F4.3,2F5.4,11(A5,F6.0))
C
      DO 21 KSTL=1,8
      IF(KOMP(STALOC(1,KSTL),1,STA,1,8).EQ.0)GO TO 22
   21 CONTINUE
      WRITE(108,12),STA
   12 FORMAT(*STATION CODE *,A8,* DOES NOT EXIST*)
      GO TO 35
C
   22 CF=TIME*(FSTOP+FSTRT)/2.
      PARTS=(GRSS-TARE)/(PRESS*CF)*BFAC
C
      DO 24 I=1,11
      POL=P(I)
      NGRMS=Q(I)
```

```
59.           DO 23 KPLT=1,11
60.           IF(KOMP(POLUTS(1,KPLT),1,POL,1,8).EQ.0)GO TO 24
61.        23 CONTINUE
62.           WRITE(108,13),POL
63.        13 FORMAT($POLLUTANT CODE $,A8,$ DOES NOT EXIST$)
64.           GO TO 35
65.        24 PGRMS(KSTL,KPLT)=NGRMS/(PRESS*CF*AFAC)
66.     C
67.           KDC(KSTL)=KDC(KSTL)+1
68.           DO 28 I=1,11
69.        28 DGPST(I+2,KDC(KSTL),KSTL)=PGRMS(KSTL,I)
70.           CALL MOVE(DATE,1,DGPST(1,KDC(KSTL),KSTL),1,8)
71.           DGPST(14,KDC(KSTL),KSTL)=PARTS
72.     C
73.           WRITE(108,14),CODE,(STALOC(I,KSTL),I=1,7),DATE(1),DATE,PARTS,
74.          *(O,(POLUTS(I,K),I=1,7),PGRMS(KSTL,K),PGRMS(KSTL,K),
75.          *(CCLS(I,K),I=1,2),K=1,11)
76.        14 FORMAT(1H1,T43,$AIRBORNE PESTICIDE DATA$,//,T49,*CODING FORM$,///,
77.          *T107,$CARD COLUMNS$,/,T107,12$-$,///,T83,$PROGRAM CODE$,/,
78.          *T89,A1,T110,$(  1  )$,//,T89,$-$,4/,
79.          *T19,$STATION NAME$,T50,$STATION CODE$,
80.          *T70,$SAMPLE DATE$,///,T52,2A4,T17,5A4,T71,A2,$/$,R2,$/$,A2,
81.          *T110,$( 2-15)$,//,T52,8$-$,T71,$-- -- --$,5/,
82.          *T18,$SUSPENDED PARTICULATE MATTER$,T65,$TIME$,
83.          *T75,$CLASS$,T86,$SOURCE$,///,T25,F7.2,T40,$UG/CM*,
84.          *T67,$7$,T77,$9$,T88,$99$,
85.          *T110,$(16-19)$,//,T67,$-$,T77,$-$,T88,$--$,6/,
86.          *T7,$NAME OF$,T32,$MEASURE$,T45,*POLLUTANT$,
87.          *T60,$SAMPLING$,T74,$MEASURED$,T88,$DECIMAL$,//,T6,*POLLUTANT$,
88.          *T33,$UNITS$,T47,$CODE$,T61,$METHOD$,T75,$VALUE$,T88,$POSITION$,///,
89.          *IO,(5(T47,2A4,T33,$NG/CM$,T6,5A4,T63,$99$,
90.          *T76,+4P,E9.0,-2X,E9.0,T80,11$ $,OP,
91.          *T110,$($,I2,$-$,I2,$)$,IO,/)))
92.           WRITE(108,16)
93.        16 FORMAT(T47,5$-$,T63,$--$,T76,4$-$,T91,$-$)
94.           GO TO 20
95.     C
96.        30 DO 25, I=1,11
97.        25 WRITE(108,15),(POLUTS(K,I),K=1,7),DATE(1),DATE,
98.          *((STALOC(K,J),K=3,7),PGRMS(J,I),J=1,8)
99.        15 FORMAT(1H1,T36,$AIRBORNE PESTICIDE DATA$,//,
100.         *                                    T39,$VALUE BY STATION$,///,
101.         *T9,*PESTICIDE NAME$,T42,$PESTICIDE CODE$,T68,$SAMPLING DATE$,///,
102.         *T45,2A4,T9,5A4,T70,A2,$/$,R2,$/$,A2,/////,T21,$STATION NAME$,
103.         *T50,$VALUE  NG/CM$,///,
104.         *(T19,5A4,T50,F10.4))
105.    C
106.          CALL BUFFERIN(1,0,FILE,41,N)
107.       38 GO TO (38,20,35,20),N
108.       35 WRITE(108,18),((STALOC(L,K),L=1,7),KDC(K),(DGPST(1,J,K),
109.         *(DGPST(I,J,K),I=1,14),J=1,KDC(K)),K=1,8)
110.       18 FORMAT((1H1,T52,$AIRBORNE PESTICIDE DATA$/T57,$VALUE BY DATE$,//,
111.         *T61,$NG/CM$,4/,
112.         *T18,$STATION CODE :  $,2A4,//,T18$STATION NAME :  $,5A4,////,
113.         *T74,$HEPTA-$,T94,$METHYL$,T124,$SUSP.$,T2,12(9X$I$),//,
114.         *T44$HEPTA-$,T74,$CLOR   | MALA-  | PARA-  | PARA-  | TOTAL  |
115.         * PART.$,T2,7(9X,$I$),//,
116.         *T4$DATE   | ALDRIN |   DDD   |   DDT   |  CLOR  |   DDE   | END
117.         *RIN |$,
```

```
118.          *T73,$EPOXIDE | THION | THION | THION | 2,4-D | MATTER$,//
119.          *N(T2,12(9X,$|$),T2,A2,$/$,R2,$/$,A2,T11,12(9|$,F7.2,2X)/)))
120.           CALL EXIT
121.           END
```

NAME	TYPE	CLASS	HEX LOC	DEC WORDS
AFAC	R	SCALR	00C13 V	1
CCLS	I	ARRAY	00CA1 V	22
DATE	I	ARRAY	00C9F V	2
FILE	I	ARRAY	00000 V	41
GRSS	R	SCALR	00C0E V	1
K	I	SCALR	00C8C V	1
KPLT	I	SCALR	00C88 V	1
MBVE		SPROG	EXTERN	
P	D	ARRAY	00039 V	22
PBL	D	SCALR	00C18 V	2
Q	R	ARRAY	00029 V	11
TARE	R	SCALR	00C0D V	1

NAME	TYPE	CLASS	HEX LOC	DEC WORDS
BFAC	R	SCALR	00C14 V	1
CF	R	SCALR	00C12 V	1
DOPST	R	ARRAY	0009A V	2912
FSTOP	R	SCALR	00C0C V	1
I	I	SCALR	00C87 V	1
KDC	R	ARRAY	008AA V	8
KSTL	I	SCALR	00C8A V	1
N	I	SCALR	00C88 V	1
PARTS	R	SCALR	00C11 V	1
PBLUTS	I	ARRAY	00C52 V	77
STA	D	SCALR	00C16 V	2
TIME	R	SCALR	00C0A V	1

NAME	TYPE	CLASS	HEX LOC	DEC WORDS
BUFFERIN		SPROG	EXTERN	
CODE	I	SCALR	00CB9 V	1
EXIT		SPROG	EXTERN	
FSTRT	R	SCALR	00C08 V	1
J	I	SCALR	00C8D V	1
KBMP	I	SPROG	EXTERN	
L	I	SCALR	00C8E V	1
NGRMS	R	SCALR	00C10 V	1
PGRMS	R	ARRAY	00882 V	84
PRESS	R	SCALR	00C0F V	1
STALOC	I	ARRAY	00C1A V	54

LABEL	HEX LOC	LABEL	HEX LOC	LABEL	HEX LOC	LABEL	HEX LOC	LABEL	HEX LOC	LABEL	HEX LOC
10	00038	12	00060	19	0009A	14	00128	15	00227	16	001E6
18	002A5	20	00000	21	00058	22	0006C	23	00090	24	000A6
25	001F4	27	00009	28	00088	30	001F1	35	00272	36	00014
37	0001D	38	00269								

LOCAL VARIABLES (3263 WORDS):

00000 FILE	00029 Q	00034 P	0004A DOPST	008AA KDC	00882 PGRMS
00C0A TIME	00C08 FSTRT	00C0C FSTOP	00C0D TARE	00C0E GRSS	00C0F PRESS
00C10 NGRMS	00C11 PARTS	00C12 CF	00C13 AFAC	00C14 BFAC	00C16 STA
00C18 PBL	00C1A STALOC	00C52 PBLUTS	00C9F DATE	00CA1 CCLS	00C87 I
00C88 N	00C89 CODE	00C8A KSTL	00C88 KPLT	00C8C K	00C8D J
00C8E L					

BLANK COMMON (0 WORDS)

EXTERNAL SUBPROGRAMS REQUIRED:

BUFFERIN	EXIT	KBMP	MBVE	FIIO8	MIO8	MIAC	9DECODE
9ENDIBL	9INITIAL	9IBDATA	9IALUSA	9PRINT	9RTBI	9STOP	

HIGHEST ERROR SEVERITY: 0 (NO ERRORS)

	DEC WORDS	HEX WORDS
GENERATED CODE:	801	00321
CONSTANTS:	8	00008
LOCAL VARIABLES:	3263	00CBF
TEMPS:	3	00003
TOTAL PROGRAM:	4075	00FEB

SECTION

APPENDIX H

REFERENCES

1. Pesticide Analytical Manual Volume I "Methods Which Detect Multiple Residues" Food and Drug Administration, U.S. Department of Health, Education and Welfare, Washington, D. C. (1971).

2. Thompson, J. F., Editor, "Analysis of Pesticide Residues in Human and Environmental Samples," Perrine Primate Research Laboratories, Environmental Protection Agency, Perrine, Florida (1971).

3. Hall, E. T., "Variations of Florisil Activity: Method to Increase Retentive Properties and Improve Recovery and Elution Patterns of Insecticides," JAOAC, 54 (6), 1349 - 1351, 1971.

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